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| (21) International Application Number: PCT/IB99/00470 (22) International Filing Date: 22 March 1999 (22.03.99) (30) Priority Data: 98870057.1 23 March 1998 (23.03.98) EP (71) Applicant (for all designated States except US): THE PROCTER & GAMBLE COMPANY [US/US]; One Procter & Gamble Plaza, Cincinnati, OH 45202 (US). (72) Inventors; and (75) Inventors/Applicants (for US only): DEPOOT, Karel, Jozef, Maria [BE/BE]; Boulezlaan 9, B-8790 Waregem (BE). DE BUZZACCARINI, Francesco [IT/BE]; Koningin Astridlaan 5, B-2870 Breendonk (BE). DELPLANCKE, Patrick, Firmin, August [BE/BE]; Dendermondsesteenweg 797, B-9070 Destelbergen (BE). (74) Agents: REED, T., David et al.; The Procter & Gamble Company, 5299 Spring Grove Avenue, Cincinnati, OH 45217-1087 (US). | | (81) Designated States: AL, AM, AT, AT (Utility model), AU, AZ, BA, BB, BG, BR, BY, CA, CH, CN, CU, CZ, CZ (Utility model), DE, DE (Utility model), DK, DK (Utility model), EE, EE (Utility model), ES, FI, FI (Utility model), GB, GD, GE, GH, GM, HR, HU, ID, IL, IN, IS, JP, KE, KG, KP, KR, KZ, LC, LK, LR, LS, LT, LU, LV, MD, MG, MK, MN, MW, MX, NO, NZ, PL, PT, RO, RU, SD, SE, SG, SI, SK, SK (Utility model), SL, TJ, TM, TR, TT, UA, UG, US, UZ, VN, YU, ZW, ARIPO patent (GH, GM, KE, LS, MW, SD, SL, SZ, UG, ZW), Eurasian patent (AM, AZ, BY, KG, KZ, MD, RU, TJ, TM), European patent (AT, BE, CH, CY, DE, DK, ES, FI, FR, GB, GR, IE, IT, LU, MC, NL, PT, SE), OAPI patent (BF, BJ, CF, CG, CI, CM, GA, GN, GW, ML, MR, NE, SN, TD, TG). Published <i>With international search report.</i> |
| (54) Title: LIQUID LAUNDRY DETERGENT COMPOSITIONS COMPRISING HEDP AND POLYAMINES (57) Abstract <p>Liquid laundry detergent compositions comprising HEDP, and water soluble and/or dispersible, modified polyamines having functionalized backbone moieties which provide a stabilizing effect.</p> | | |

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LIQUID LAUNDRY DETERGENT COMPOSITIONS COMPRISING HEDP AND POLYAMINES

FIELD OF THE INVENTION

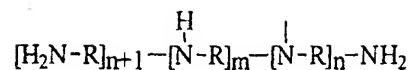
The present invention relates to liquid laundry detergent compositions comprising HEDP and water soluble and/or dispersible, modified polyamines having functionalized backbone moieties.

BACKGROUND OF THE INVENTION

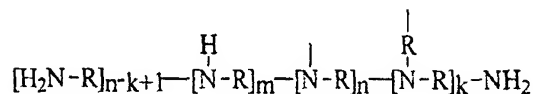
Liquid laundry detergent compositions comprising HEDP (hydroxyethane-1,1-diphosphonate) are known and have been described for instance in FR 2,677,370, EP 517 605, EP 384 515, and EP 37 184. In liquid laundry detergent compositions, HEDP provides benefits of improved stain removal and whiteness on fabrics. However there is an issue in formulating HEDP in liquid detergents - particularly concentrated ones - in that poor physical stability is obtained in the presence of high levels of surfactants and other detergent ingredients. EP 517 605 discloses the use of specific salts of HEDP in order to improve the physical stability of the composition. It is an object of the present invention to formulate liquid detergent compositions which comprise HEDP and surfactants and, optionally other detergency ingredients, and, which are physically stable. In response, it has now been found that the presence of certain polymers would provide the desired stabilizing effect enabling the formulation of stable compositions comprising HEDP.

SUMMARY OF THE INVENTION

The present invention encompasses liquid laundry detergent compositions comprising a surfactant, an effective amount of HEDP, and a stabilizing amount of a water-soluble or dispersible, modified polyamine comprising a polyamine backbone corresponding to the formula:

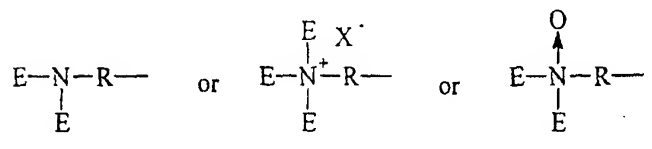


having a modified polyamine formula $V_{(n+1)}W_mY_nZ$ or a polyamine backbone corresponding to the formula:

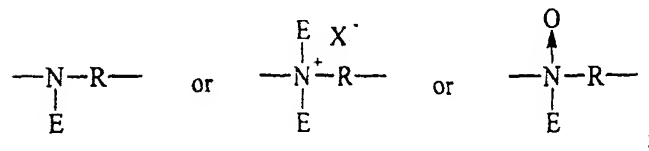


having a modified polyamine formula $V_{(n-k+1)}W_mY_nY'_kZ$, wherein k is less than or equal to n , said polyamine backbone prior to modification has a molecular weight greater than about 200 daltons, wherein

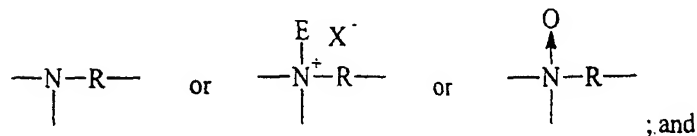
i) V units are terminal units having the formula:



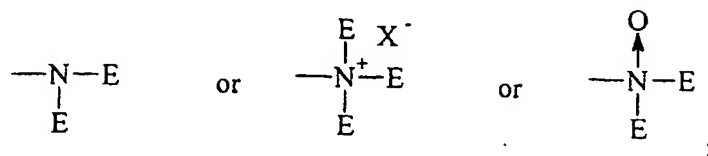
ii) W units are backbone units having the formula:



iii) Y units are branching units having the formula:



iv) Z units are terminal units having the formula:



wherein backbone linking R units are selected from the group consisting of C₂-C₁₂ alkylene, C₄-C₁₂ alkenylene, C₃-C₁₂ hydroxyalkylene, C₄-C₁₂ dihydroxy-alkylene, C₈-C₁₂ dialkylarylene, $-(R^1O)_xR^1-$, $-(R^1O)_xR^5(OR^1)_x-$, $-(CH_2CH(OR^2)CH_2O)(R^1O)_y-$, $R^1O(CH_2CH(OR^2)CH_2)_w-$, $-C(O)(R^4)_rC(O)-$, $-CH_2CH(OR^2)CH_2-$, and mixtures thereof; wherein R¹ is C₂-C₆ alkylene and mixtures thereof; R² is hydrogen, $-(R^1O)_xB$, and mixtures thereof; R³ is C₁-C₁₈ alkyl, C₇-C₁₂ arylalkyl, C₇-C₁₂ alkyl substituted aryl, C₆-C₁₂ aryl, and mixtures thereof; R⁴ is C₁-C₁₂ alkylene, C₄-C₁₂ alkenylene, C₈-C₁₂ arylalkylene, C₆-C₁₀ arylene, and mixtures thereof; R⁵ is C₁-C₁₂ alkylene, C₃-C₁₂ hydroxy-alkylene, C₄-C₁₂ dihydroxyalkylene, C₈-C₁₂ dialkylarylene, $-C(O)-$, $-C(O)NHR^6-NHC(O)-$, $-C(O)(R^4)_rC(O)-$, $-CH_2CH(OH)CH_2O(R^1O)_yR^1O-CH_2CH(OH)CH_2-$, and mixtures thereof; R⁶ is C₂-C₁₂ alkylene or C₆-C₁₂ arylene; E units are selected from the group consisting of hydrogen, C₁-C₂₂ alkyl, C₃-C₂₂ alkenyl, C₇-C₂₂ arylalkyl, C₂-C₂₂ hydroxyalkyl, $-(CH_2)_pCO_2M$, $(CH_2)_qSO_3M$, $-CH(CH_2CO_2M)-CO_2M$, $-(CH_2)_pPO_3M$, $-(R^1O)_xB$, $-C(O)R^3$, and mixtures thereof; provided that when any E unit of a nitrogen is a hydrogen, said nitrogen is not also an N-oxide; B is hydrogen, C₁-C₆ alkyl, $-(CH_2)_qSO_3M$, $-(CH_2)_pCO_2M$, $(CH_2)_qCH(SO_3M)CH_2SO_3M$, $-(CH_2)_qCH(SO_2M)CH_2SO_3M$, $(CH_2)_pPO_3M$, $-PO_3M$, and mixtures thereof; M is hydrogen or a water soluble cation in sufficient amount to satisfy charge balance; X is a water soluble anion; m has the value from 4 to about 400; n has the value from 1 to about 200; p has the value from 1 to 6, q has the value from 0 to 6; r

has the value of 0 or 1; w has the value 0 or 1; x has the value from 1 to 100; y has the value from 0 to 100; z has the value 0 or 1.

All percentages, ratios and proportions herein are by weight of the total composition, unless otherwise specified. All temperatures are in degrees Celsius ($^{\circ}$ C) unless otherwise specified, and ratios are by weight. All documents cited are in relevant part, incorporated herein by reference.

DETAILED DESCRIPTION OF THE INVENTION

The liquid detergent composition

The compositions herein are liquid detergent compositions and as such, they typically but not necessarily comprise water, in amounts of from 20% to 70% by weight of the total composition, preferably 25% to 60% , most preferably 30% to 40%. Compositions comprising less than 40% water are generally referred to as concentrated compositions, and it is in those compositions that the stability problem of HEDP is particularly acute.

HEDP

The compositions herein comprise an effective amount of HEDP (hydroxyethane-1,1-diphosphonate). By effective amount, it is meant herein an amount sufficient so as to improve the stain removal properties of the detergent composition, and/or to improve the whiteness performance of that composition. Typically such amounts are in the range of from 0.01% to 10% by weight of the total composition, preferably 0.7% to 5%, most preferably 0.2% to 2%. Suitable for use herein are HEDP in its acid form, or in the form of any of its salts. A suitable commercial form of HEDP is Dequest[®]2010, from Monsanto.

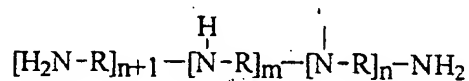
The polyamine

The compositions herein further comprise a stabilizing amount of a water-soluble or dispersible, modified polyamine. These polyamines comprise backbones that can be either linear or cyclic. The polyamine backbones can also comprise polyamine

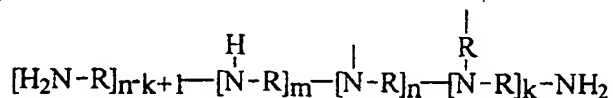
branching chains to a greater or lesser degree. In general, the polyamine backbones described herein are modified in such a manner that each nitrogen of the polyamine chain is thereafter described in terms of a unit that is substituted, quaternized, oxidized, or combinations thereof.

For the purposes of the present invention the term "modification" is defined as replacing a backbone -NH hydrogen atom by an E unit (substitution), quaternizing a backbone nitrogen (quaternized) or oxidizing a backbone nitrogen to the N-oxide (oxidized). The terms "modification" and "substitution" are used interchangeably when referring to the process of replacing a hydrogen atom attached to a backbone nitrogen with an E unit. Quaternization or oxidation may take place in some circumstances without substitution, but substitution preferably is accompanied by oxidation or quaternization of at least one backbone nitrogen.

The linear or non-cyclic polyamine backbones have the general formula:



said backbones prior to subsequent modification, comprise primary, secondary and tertiary amine nitrogens connected by R "linking" units. The cyclic polyamine backbones have the general formula:



said backbones prior to subsequent modification, comprise primary, secondary and tertiary amine nitrogens connected by R "linking" units

For the purpose of the present invention, primary amine nitrogens comprising the backbone or branching chain once modified are defined as V or Z "terminal" units. For example, when a primary amine moiety, located at the end of the main polyamine backbone or branching chain having the structure

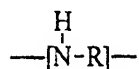


is modified according to the present invention, it is thereafter defined as a V "terminal" unit, or simply a V unit. However, for the purposes of the present invention, some or all of the primary amine moieties can remain unmodified subject to the restrictions further described herein below. These unmodified primary amine moieties by virtue of their position in the backbone chain remain "terminal" units. Likewise, when a primary amine moiety, located at the end of the main polyamine backbone having the structure



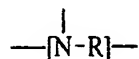
is modified according to the present invention, it is thereafter defined as a Z "terminal" unit, or simply a Z unit. This unit can remain unmodified subject to the restrictions further described herein below.

In a similar manner, secondary amine nitrogens comprising the backbone or branching chain once modified are defined as W "backbone" units. For example, when a secondary amine moiety, the major constituent of the backbones and branching chains of the present invention, having the structure



is modified according to the present invention, it is thereafter defined as a W "backbone" unit, or simply a W unit. However, for the purposes of the present invention, some or all of the secondary amine moieties can remain unmodified. These unmodified secondary amine moieties by virtue of their position in the backbone chain remain "backbone" units.

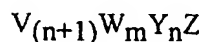
In a further similar manner, tertiary amine nitrogens comprising the backbone or branching chain once modified are further referred to as Y "branching" units. For example, when a tertiary amine moiety, which is a chain branch point of either the polyamine backbone or other branching chains or rings, having the structure



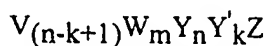
is modified according to the present invention, it is thereafter defined as a Y "branching" unit, or simply a Y unit. However, for the purposes of the present invention, some or all of the tertiary amine moieties can remain unmodified. These unmodified tertiary amine

moieties by virtue of their position in the backbone chain remain "branching" units. The R units associated with the V, W and Y unit nitrogens which serve to connect the polyamine nitrogens, are described herein below.

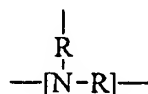
The final modified structure of the polyamines of the present invention can be therefore represented by the general formula



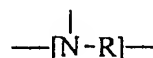
for linear polyamine cotton soil release polymers and by the general formula



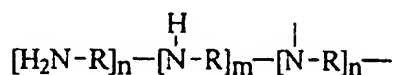
for cyclic polyamine cotton soil release polymers. For the case of polyamines comprising rings, a Y' unit of the formula



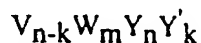
serves as a branch point for a backbone or branch ring. For every Y' unit there is a Y unit having the formula



that will form the connection point of the ring to the main polymer chain or branch. In the unique case where the backbone is a complete ring, the polyamine backbone has the formula



therefore comprising no Z terminal unit and having the formula



wherein k is the number of ring forming branching units. Preferably the polyamine backbones of the present invention comprise no rings.

In the case of non-cyclic polyamines, the ratio of the index n to the index m relates to the relative degree of branching. A fully non-branched linear modified polyamine according to the present invention has the formula

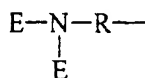


that is, n is equal to 0. The greater the value of n (the lower the ratio of m to n), the greater the degree of branching in the molecule. Typically the value for m ranges from a minimum value of 4 to about 400, however larger values of m , especially when the value of the index n is very low or nearly 0, are also preferred.

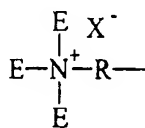
Each polyamine nitrogen whether primary, secondary or tertiary, once modified according to the present invention, is further defined as being a member of one of three general classes; simple substituted, quaternized or oxidized. Those polyamine nitrogen units not modified are classed into V, W, Y, or Z units depending on whether they are primary, secondary or tertiary nitrogens. That is unmodified primary amine nitrogens are V or Z units, unmodified secondary amine nitrogens are W units and unmodified tertiary amine nitrogens are Y units for the purposes of the present invention.

Modified primary amine moieties are defined as V "terminal" units having one of three forms:

- a) simple substituted units having the structure:

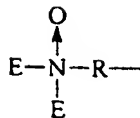


- b) quaternized units having the structure:



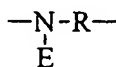
wherein X is a suitable counter ion providing charge balance; and

- c) oxidized units having the structure:

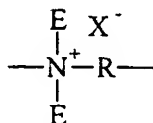


Modified secondary amine moieties are defined as W "backbone" units having one of three forms:

- a) simple substituted units having the structure:

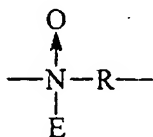


- b) quaternized units having the structure:



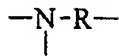
wherein X is a suitable counter ion providing charge balance; and

- c) oxidized units having the structure:

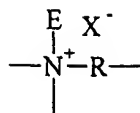


Modified tertiary amine moieties are defined as Y "branching" units having one of three forms:

- a) unmodified units having the structure:

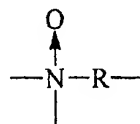


- b) quaternized units having the structure:



wherein X is a suitable counter ion providing charge balance; and

- c) oxidized units having the structure:

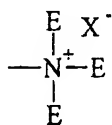


Certain modified primary amine moieties are defined as Z "terminal" units having one of three forms:

- a) simple substituted units having the structure:

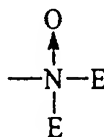


- b) quaternized units having the structure:



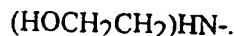
wherein X is a suitable counter ion providing charge balance; and

- c) oxidized units having the structure:



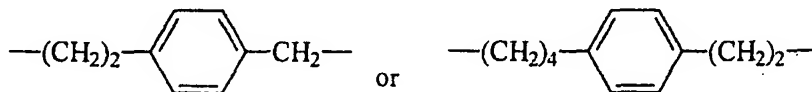
When any position on a nitrogen is unsubstituted or unmodified, it is understood that hydrogen will substitute for E. For example, a primary amine unit comprising one E

unit in the form of a hydroxyethyl moiety is a V terminal unit having the formula



For the purposes of the present invention there are two types of chain terminating units, the V and Z units. The Z "terminal" unit derives from a terminal primary amino moiety of the structure -NH_2 . Non-cyclic polyamine backbones according to the present invention comprise only one Z unit whereas cyclic polyamines can comprise no Z units. The Z "terminal" unit can be substituted with any of the E units described further herein below, except when the Z unit is modified to form an N-oxide. In the case where the Z unit nitrogen is oxidized to an N-oxide, the nitrogen must be modified and therefore E cannot be a hydrogen.

The polyamines of the present invention comprise backbone R "linking" units that serve to connect the nitrogen atoms of the backbone. R units comprise units that for the purposes of the present invention are referred to as "hydrocarbyl R" units and "oxy R" units. The "hydrocarbyl" R units are $\text{C}_2\text{-C}_{12}$ alkylene, $\text{C}_4\text{-C}_{12}$ alkenylene, $\text{C}_3\text{-C}_{12}$ hydroxyalkylene wherein the hydroxyl moiety may take any position on the R unit chain except the carbon atoms directly connected to the polyamine backbone nitrogens; $\text{C}_4\text{-C}_{12}$ dihydroxyalkylene wherein the hydroxyl moieties may occupy any two of the carbon atoms of the R unit chain except those carbon atoms directly connected to the polyamine backbone nitrogens; $\text{C}_8\text{-C}_{12}$ dialkylarylene which for the purpose of the present invention are arylene moieties having two alkyl substituent groups as part of the linking chain. For example, a dialkylarylene unit has the formula



although the unit need not be 1,4-substituted, but can also be 1,2 or 1,3 substituted $\text{C}_2\text{-C}_{12}$ alkylene, preferably ethylene, 1,2-propylene, and mixtures thereof, more preferably ethylene. The "oxy" R units comprise $\text{---}(\text{R}^1\text{O})_x\text{R}^5(\text{OR}^1)_x\text{---}$, $\text{CH}_2\text{CH}(\text{OR}^2)\text{CH}_2\text{O})_z(\text{R}^1\text{O})_y\text{R}^1(\text{OCH}_2\text{CH}(\text{OR}^2)\text{CH}_2)_w\text{---}$, $\text{---CH}_2\text{CH}(\text{OR}^2)\text{CH}_2\text{---}$, $(\text{R}^1\text{O})_x\text{R}^1\text{---}$, and mixtures thereof. Preferred R units are $\text{C}_2\text{-C}_{12}$ alkylene, $\text{C}_3\text{-C}_{12}$ hydroxyalkylene, $\text{C}_4\text{-C}_{12}$ dihydroxyalkylene, $\text{C}_8\text{-C}_{12}$ dialkylarylene, $\text{---}(\text{R}^1\text{O})_x\text{R}^1\text{---}$,

CH₂CH(OR²)CH₂-, -(CH₂CH(OH)CH₂O)_z(R¹O)_yR¹(OCH₂CH-(OH)CH₂)_w-,
 (R¹O)_xR⁵(OR¹)_x-, more preferred R units are C₂-C₁₂ alkylene, C₃-C₁₂ hydroxy-
 alkylene, C₄-C₁₂ dihydroxyalkylene, -(R¹O)_xR¹-, -(R¹O)_xR⁵(OR¹)_x-,
 (CH₂CH(OH)CH₂O)_z(R¹O)_yR¹(OCH₂CH-(OH)CH₂)_w-, and mixtures thereof, even
 more preferred R units are C₂-C₁₂ alkylene, C₃ hydroxyalkylene, and mixtures thereof,
 most preferred are C₂-C₆ alkylene. The most preferred backbones of the present
 invention comprise at least 50% R units that are ethylene.

R¹ units are C₂-C₆ alkylene, and mixtures thereof, preferably ethylene. R² is
 hydrogen, and -(R¹O)_xB, preferably hydrogen.

R³ is C₁-C₁₈ alkyl, C₇-C₁₂ arylalkylene, C₇-C₁₂ alkyl substituted aryl, C₆-C₁₂
 aryl, and mixtures thereof, preferably C₁-C₁₂ alkyl, C₇-C₁₂ arylalkylene, more
 preferably C₁-C₁₂ alkyl, most preferably methyl. R³ units serve as part of E units
 described herein below.

R⁴ is C₁-C₁₂ alkylene, C₄-C₁₂ alkenylene, C₈-C₁₂ arylalkylene, C₆-C₁₀
 arylene, preferably C₁-C₁₀ alkylene, C₈-C₁₂ arylalkylene, more preferably C₂-C₈
 alkylene, most preferably ethylene or butylene.

R⁵ is C₁-C₁₂ alkylene, C₃-C₁₂ hydroxyalkylene, C₄-C₁₂ dihydroxyalkylene,
 C₈-C₁₂ dialkylarylene, -C(O)-, -C(O)NHR⁶NHC(O)-, -C(O)(R⁴)_tC(O)-,
 -R¹(OR¹)-, -CH₂CH(OH)CH₂O(R¹O)_yR¹OCH₂CH(OH)CH₂-, -C(O)(R⁴)_tC(O)-,
 -CH₂CH(OH)CH₂-, R⁵ is preferably ethylene, -C(O)-, -C(O)NHR⁶NHC(O)-,
 -R¹(OR¹)-, -CH₂CH(OH)CH₂-, -CH₂CH(OH)CH₂O(R¹O)_yR¹OCH₂CH-(OH)CH₂-,
 more preferably -CH₂CH(OH)CH₂-.

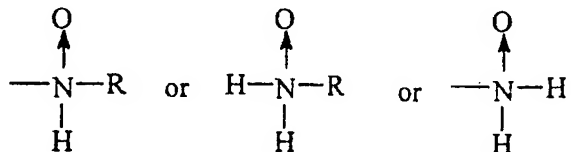
R⁶ is C₂-C₁₂ alkylene or C₆-C₁₂ arylene.

The preferred "oxy" R units are further defined in terms of the R¹, R², and R⁵
 units. Preferred "oxy" R units comprise the preferred R¹, R², and R⁵ units. The
 preferred cotton soil release agents of the present invention comprise at least 50% R¹
 units that are ethylene. Preferred R¹, R², and R⁵ units are combined with the "oxy" R
 units to yield the preferred "oxy" R units in the following manner.

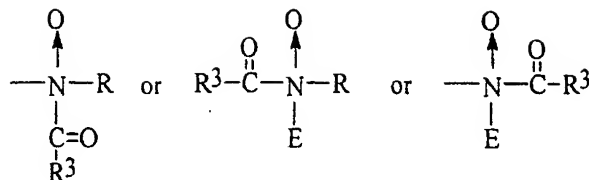
- i) Substituting more preferred R^5 into $-(CH_2CH_2O)_xR^5(OCH_2CH_2)_x-$ yields $-(CH_2CH_2O)_xCH_2CHOHCH_2(OCH_2CH_2)_x-$.
- ii) Substituting preferred R^1 and R^2 into $-(CH_2CH(OR^2)CH_2O)_z-(R^1O)_yR^1O(CH_2CH(OR^2)CH_2)_w-$ yields $-(CH_2CH(OH)CH_2O)_z-(CH_2CH_2O)_yCH_2CH_2O(CH_2CH(OH)CH_2)_w-$.
- iii) Substituting preferred R^2 into $-CH_2CH(OR^2)CH_2-$ yields $-CH_2CH(OH)CH_2-$.

E units are selected from the group consisting of hydrogen, C_1 - C_{22} alkyl, C_3 - C_{22} alkenyl, C_7 - C_{22} arylalkyl, C_2 - C_{22} hydroxyalkyl, $-(CH_2)_pCO_2M$, $-(CH_2)_qSO_3M$, $-CH(CH_2CO_2M)CO_2M$, $-(CH_2)_pPO_3M$, $-(R^1O)_mB$, $-C(O)R^3$, preferably hydrogen, C_2 - C_{22} hydroxyalkylene, benzyl, C_1 - C_{22} alkylene, $-(R^1O)_mB$, $-C(O)R^3$, $-(CH_2)_pCO_2M$, $-(CH_2)_qSO_3M$, $-CH(CH_2CO_2M)CO_2M$, more preferably C_1 - C_{22} alkylene, $-(R^1O)_xB$, $-C(O)R^3$, $-(CH_2)_pCO_2M$, $-(CH_2)_qSO_3M$, $-CH(CH_2CO_2M)CO_2M$, most preferably C_1 - C_{22} alkylene, $-(R^1O)_xB$, and $-C(O)R^3$. When no modification or substitution is made on a nitrogen then hydrogen atom will remain as the moiety representing E.

E units do not comprise hydrogen atom when the V, W or Z units are oxidized, that is the nitrogens are N-oxides. For example, the backbone chain or branching chains do not comprise units of the following structure:



Additionally, E units do not comprise carbonyl moieties directly bonded to a nitrogen atom when the V, W or Z units are oxidized, that is, the nitrogens are N-oxides. According to the present invention, the E unit $-C(O)R^3$ moiety is not bonded to an N-oxide modified nitrogen, that is, there are no N-oxide amides having the structure



nor combinations thereof.

B is hydrogen, C₁-C₆ alkyl, -(CH₂)_qSO₃M, -(CH₂)_pCO₂M, -(CH₂)_q-(CHSO₃M)CH₂SO₃M, -(CH₂)_q(CHSO₂M)CH₂SO₃M, -(CH₂)_pPO₃M, -PO₃M, preferably hydrogen, -(CH₂)_qSO₃M, -(CH₂)_q(CHSO₃M)CH₂SO₃M, -(CH₂)_q-(CHSO₂M)CH₂SO₃M, more preferably hydrogen or -(CH₂)_qSO₃M.

M is hydrogen or a water soluble cation in sufficient amount to satisfy charge balance. For example, a sodium cation equally satisfies -(CH₂)_pCO₂M, and -(CH₂)_qSO₃M, thereby resulting in -(CH₂)_pCO₂Na, and -(CH₂)_qSO₃Na moieties. More than one monovalent cation, (sodium, potassium, etc.) can be combined to satisfy the required chemical charge balance. However, more than one anionic group may be charge balanced by a divalent cation, or more than one mono-valent cation may be necessary to satisfy the charge requirements of a poly-anionic radical. For example, a -(CH₂)_pPO₃M moiety substituted with sodium atoms has the formula -(CH₂)_pPO₃Na₃. Divalent cations such as calcium (Ca²⁺) or magnesium (Mg²⁺) may be substituted for or combined with other suitable mono-valent water soluble cations. Preferred cations are sodium and potassium, more preferred is sodium.

X is a water soluble anion such as chlorine (Cl⁻), bromine (Br⁻) and iodine (I⁻) or X can be any negatively charged radical such as sulfate (SO₄²⁻) and methosulfate (CH₃SO₃⁻).

The formula indices have the following values: p has the value from 1 to 6, q has the value from 0 to 6; r has the value 0 or 1; w has the value 0 or 1, x has the value from 1 to 100, preferably 5 to 30; y has the value from 0 to 100; z has the value 0 or 1; m has the value from 4 to about 400, n has the value from 0 to about 200; m + n has the value of at least 5.

The preferred polyamines of the present invention comprise backbones wherein less than about 50% of the R groups comprise "oxy" R units, preferably less than about 20% , more preferably less than 5%, most preferably the R units comprise no "oxy" R units.

The most preferred polyamines which comprise no "oxy" R units comprise backbones wherein less than 50% of the R groups comprise more than 3 carbon atoms. For example, ethylene, 1,2-propylene, and 1,3-propylene comprise 3 or less carbon atoms and are the preferred "hydrocarbyl" R units. That is when backbone R units are C₂-C₁₂ alkylene, preferred is C₂-C₃ alkylene, most preferred is ethylene.

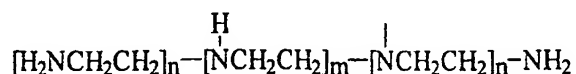
The cotton polyamines of the present invention comprise modified homogeneous and non-homogeneous polyamine backbones, wherein 100% or less of the -NH units are modified. For the purpose of the present invention the term "homogeneous polyamine backbone" is defined as a polyamine backbone having R units that are the same (i.e., all ethylene). However, this sameness definition does not exclude polyamines that comprise other extraneous units comprising the polymer backbone which are present due to an artifact of the chosen method of chemical synthesis. For example, it is known to those skilled in the art that ethanolamine may be used as an "initiator" in the synthesis of polyethyleneimines, therefore a sample of polyethyleneimine that comprises one hydroxyethyl moiety resulting from the polymerization "initiator" would be considered to comprise a homogeneous polyamine backbone for the purposes of the present invention. A polyamine backbone comprising all ethylene R units wherein no branching Y units are present is a homogeneous backbone. A polyamine backbone comprising all ethylene R units is a homogeneous backbone regardless of the degree of branching or the number of cyclic branches present.

For the purposes of the present invention the term "non-homogeneous polymer backbone" refers to polyamine backbones that are a composite of various R unit lengths and R unit types. For example, a non-homogeneous backbone comprises R units that are a mixture of ethylene and 1,2-propylene units. For the purposes of the present invention a mixture of "hydrocarbyl" and "oxy" R units is not necessary to provide a non-homogeneous backbone.

Preferred polyamines of the present invention comprise homogeneous polyamine backbones that are totally or partially substituted by polyethyleneoxy moieties, totally or partially quaternized amines, nitrogens totally or partially oxidized to N-oxides, and mixtures thereof. However, not all backbone amine nitrogens must be modified in the same manner, the choice of modification being left to the specific needs of the formulator. The degree of ethoxylation is also determined by the specific requirements of the formulator.

The preferred polyamines that comprise the backbone of the compounds of the present invention are generally polyalkyleneamines (PAA's), polyalkyleneimines (PAI's), preferably polyethyleneamine (PEA's), polyethyleneimines (PEI's), or PEA's or PEI's connected by moieties having longer R units than the parent PAA's, PAI's, PEA's or PEI's. A common polyalkyleneamine (PAA) is tetrabutylpentamine. PEA's are obtained by reactions involving ammonia and ethylene dichloride, followed by fractional distillation. The common PEA's obtained are triethylenetetramine (TETA) and tetraethylenepentamine (TEPA). Above the pentamines, i.e., the hexamines, heptamines, octamines and possibly nonamines, the cogenerically derived mixture does not appear to separate by distillation and can include other materials such as cyclic amines and particularly piperazines. There can also be present cyclic amines with side chains in which nitrogen atoms appear. See U.S. Patent 2,792,372, Dickinson, issued May 14, 1957, which describes the preparation of PEA's.

Preferred amine polymer backbones comprise R units that are C₂ alkylene (ethylene) units, also known as polyethylenimines (PEI's). Preferred PEI's have at least moderate branching, that is the ratio of m to n is less than 4:1, however PEI's having a ratio of m to n of about 2:1 are most preferred. Preferred backbones, prior to modification have the general formula:



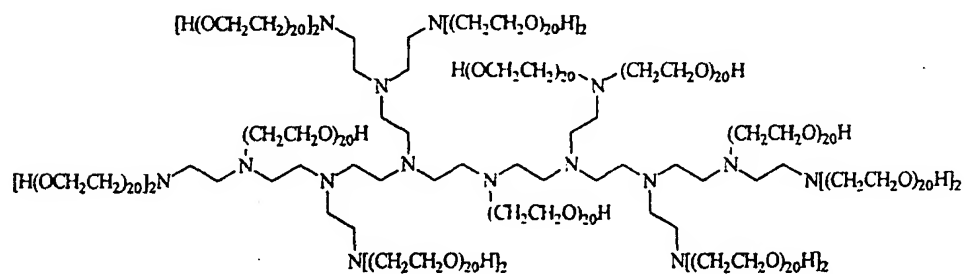
wherein m and n are the same as defined herein above. Preferred PEI's, prior to modification, will have a molecular weight greater than about 200 daltons, preferably up to 3000.

The relative proportions of primary, secondary and tertiary amine units in the polyamine backbone, especially in the case of PEI's, will vary, depending on the manner of preparation. Each hydrogen atom attached to each nitrogen atom of the polyamine backbone chain represents a potential site for subsequent substitution, quaternization or oxidation.

These polyamines can be prepared, for example, by polymerizing ethyleneimine in the presence of a catalyst such as carbon dioxide, sodium bisulfite, sulfuric acid, hydrogen peroxide, hydrochloric acid, acetic acid, etc. Specific methods for preparing these polyamine backbones are disclosed in U.S. Patent 2,182,306, Ulrich et al., issued December 5, 1939; U.S. Patent 3,033,746, Mayle et al., issued May 8, 1962; U.S. Patent 2,208,095, Esselmann et al., issued July 16, 1940; U.S. Patent 2,806,839, Crowther, issued September 17, 1957; and U.S. Patent 2,553,696, Wilson, issued May 21, 1951; all herein incorporated by reference.

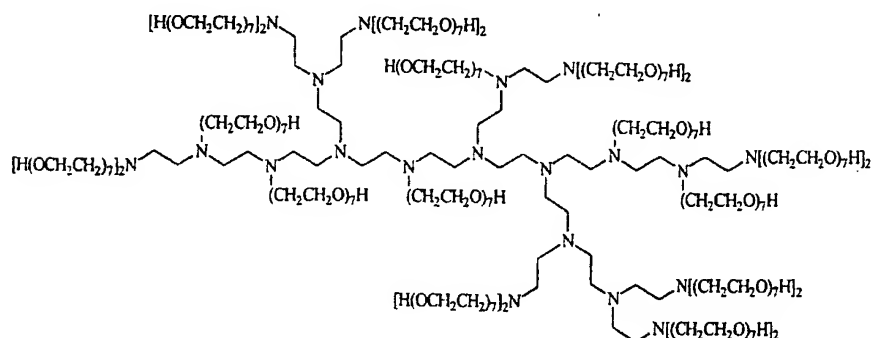
Examples of polyamines of the present invention comprising PEI's, are illustrated in Formulas I - V:

Formula I depicts a preferred polyamines comprising a PEI backbone wherein all substitutable nitrogens are modified by replacement of hydrogen with a polyoxyalkyleneoxy unit, $-(CH_2CH_2O)_{20}H$, having the formula:



Formula I

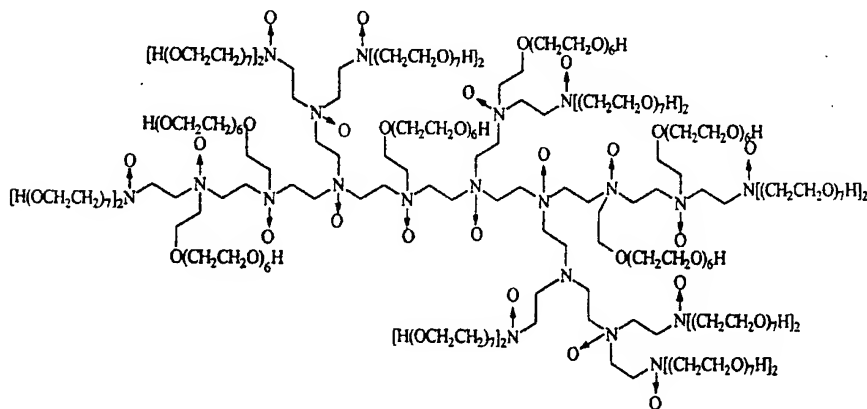
Formula II depicts a polyamine comprising a PEI backbone wherein all substitutable nitrogens are modified by replacement of hydrogen with a polyoxyalkyleneoxy unit, $-(\text{CH}_2\text{CH}_2\text{O})_7\text{H}$, having the formula



Formula II

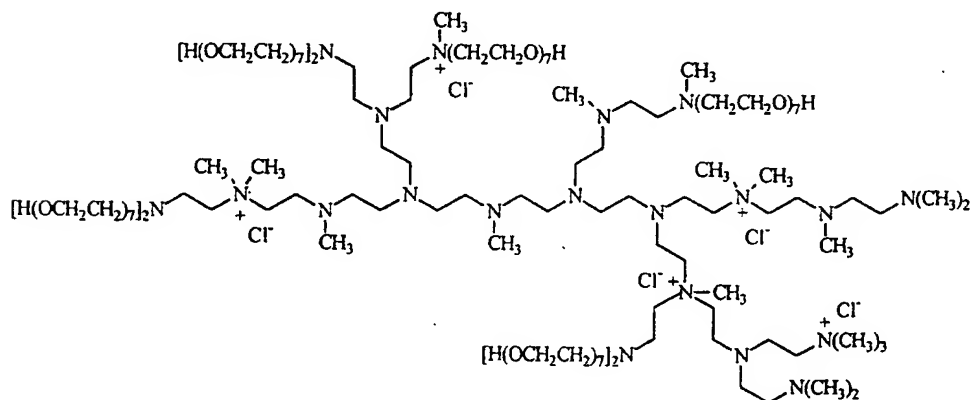
This is an example of a polyamine that is fully modified by one type of moiety.

Formula III depicts a polyamine comprising a PEI backbone wherein all substitutable primary amine nitrogens are modified by replacement of hydrogen with a polyoxyalkyleneoxy unit, $-(\text{CH}_2\text{CH}_2\text{O})_7\text{H}$, the molecule is then modified by subsequent oxidation of all oxidizable primary and secondary nitrogens to N-oxides, said polyamine having the formula



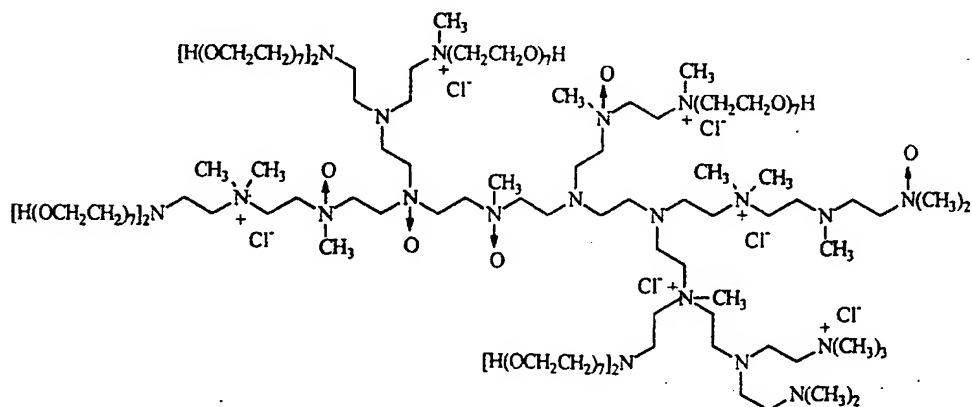
Formula III

Formula IV depicts a polyamine comprising a PEI backbone wherein all backbone hydrogen atoms are substituted and some backbone amine units are quaternized. The substituents are polyoxyalkyleneoxy units, $-(\text{CH}_2\text{CH}_2\text{O})_7\text{H}$, or methyl groups. The modified PEI polyamine has the formula



Formula IV

Formula V depicts a polyamine comprising a PEI backbone wherein the backbone nitrogens are modified by substitution (i.e. by $-(\text{CH}_2\text{CH}_2\text{O})_7\text{H}$ or methyl), quaternized, oxidized to N-oxides or combinations thereof. The resulting polyamine has the formula



Formula V

In the above examples, not all nitrogens of a unit class comprise the same modification. The present invention allows the formulator to have a portion of the secondary amine nitrogens ethoxylated while having other secondary amine nitrogens oxidized to N-oxides. This also applies to the primary amine nitrogens, in that the formulator may choose to modify all or a portion of the primary amine nitrogens with one or more substituents prior to oxidation or quaternization. Any possible combination of E groups can be substituted on the primary and secondary amine nitrogens, except for the restrictions described herein above.

Highly preferred for use herein are ethoxylated PEIs with a molecular weight of from 200 to 3000, preferably 400 to 700, and an average degree of ethoxylation of from 4 to 30, preferably 15 to 25.

The compositions herein comprise a stabilizing amount of a polyamine, i.e. an amount which is sufficient to solve the instability problem caused by the presence of the HEDP. The amount of polyamine needed will depend on the amount of HEDP which is present, but will typically lie in the range of from 0.05% to 20% by weight of the total composition, preferably 0.1% to 10%, most preferably 0.2% to 5%. In addition, the polyamines herein have the advantage that they provide stain removal and whiteness benefits.

The deterative surfactants

The compositions herein comprise a surfactant. In addition to the preferred anionic and nonionic deterative surfactants described herein, other deterative surfactants that are suitable for use in the present invention are cationic, anionic, nonionic, ampholytic, zwitterionic, and mixtures thereof, further described herein below.

Nonlimiting examples of other surfactants useful herein typically at levels from about 1% to about 55%, by weight, include the conventional C₁₁-C₁₈ alkyl benzene sulfonates ("LAS"), the C₁₀-C₁₈ secondary (2,3) alkyl sulfates of the formula

$\text{CH}_3(\text{CH}_2)_x(\text{CHOSO}_3^-\text{M}^+) \text{CH}_3$ and $\text{CH}_3(\text{CH}_2)_y(\text{CHOSO}_3^-\text{M}^+) \text{CH}_2\text{CH}_3$ where x and $(y + 1)$ are integers of at least about 7, preferably at least about 9, and M is a water-solubilizing cation, especially sodium, unsaturated sulfates such as oleyl sulfate, C_{10} - C_{18} alkyl alkoxy carboxylates (especially the EO 1-5 ethoxycarboxylates), the C_{10} - C_{18} glycerol ethers, the C_{10} - C_{18} alkyl polyglycosides and their corresponding sulfated polyglycosides, and C_{12} - C_{18} alpha-sulfonated fatty acid esters. If desired, the conventional nonionic and amphoteric surfactants such as the C_{12} - C_{18} alkyl ethoxylates ("AE") including the so-called narrow peaked alkyl ethoxylates and C_6 - C_{12} alkyl phenol alkoxyates (especially ethoxylates and mixed ethoxy/propoxy), C_{12} - C_{18} betaines and sulfobetaines ("sultaines"), C_{10} - C_{18} amine oxides, and the like, can also be included in the overall compositions. The C_{10} - C_{18} N-alkyl polyhydroxy fatty acid amides can also be used. Typical examples include the C_{12} - C_{18} N-methylglucamides. See WO 9,206,154. Other sugar-derived surfactants include the N-alkoxy polyhydroxy fatty acid amides, such as C_{10} - C_{18} N-(3-methoxypropyl) glucamide. C_{10} - C_{20} conventional soaps may also be used. If high sudsing is desired, the branched-chain C_{10} - C_{16} soaps may be used. Mixtures of anionic and nonionic surfactants are especially useful. Other conventional useful surfactants are listed in standard texts.

Other anionic surfactants useful for deterative purposes can also be included in the compositions hereof. These can include salts (including, for example, sodium potassium, ammonium, and substituted ammonium salts such as mono-, di- and triethanolamine salts) of soap, C_9 - C_{20} linear alkylbenzenesulphonates, C_8 - C_{22} primary or secondary alkanesulphonates, C_8 - C_{24} olefinsulphonates, sulphonated polycarboxylic acids, alkyl glycerol sulfonates, fatty acyl glycerol sulfonates, fatty oleyl glycerol sulfates, alkyl phenol ethylene oxide ether sulfates, paraffin sulfonates, alkyl phosphates, isothionates such as the acyl isothionates, N-acyl taurates, fatty acid amides of methyl tauride, alkyl succinates and sulfosuccinates, monoesters of sulfosuccinate (especially saturated and unsaturated C_{12} - C_{18} monoesters) diesters of sulfosuccinate (especially saturated and unsaturated C_6 - C_{14} diesters), N-acyl sarcosinates, sulfates of alkylpolysaccharides such as the sulfates of alkylpolyglucoside, branched primary alkyl sulfates, alkyl polyethoxy carboxylates such as those of the formula $\text{RO}(\text{CH}_2\text{CH}_2\text{O})_k\text{CH}_2\text{COO}-\text{M}^+$ wherein R is a

C₈-C₂₂ alkyl, k is an integer from 0 to 10, and M is a soluble salt-forming cation, and fatty acids esterified with isethionic acid and neutralized with sodium hydroxide. Further examples are given in Surface Active Agents and Detergents (Vol. I and II by Schwartz, Perry and Berch).

The compositions of the present invention preferably comprise at least about 0.01%, preferably at least 0.1%, more preferably from about 1% to about 95%, most preferably from about 1% to about 80% by weight, of an anionic deterative surfactant. Alkyl sulfate surfactants, either primary or secondary, are a type of anionic surfactant of importance for use herein. Alkyl sulfates have the general formula ROSO₃M wherein R preferably is a C₁₀-C₂₄ hydrocarbyl, preferably an alkyl straight or branched chain or hydroxyalkyl having a C₁₀-C₂₀ alkyl component, more preferably a C₁₂-C₁₈ alkyl or hydroxyalkyl, and M is hydrogen or a water soluble cation, e.g., an alkali metal cation (e.g., sodium potassium, lithium), substituted or unsubstituted ammonium cations such as methyl-, dimethyl-, and trimethyl ammonium and quaternary ammonium cations, e.g., tetramethyl-ammonium and dimethyl piperdinium, and cations derived from alkanolamines such as ethanolamine, diethanolamine, triethanolamine, and mixtures thereof, and the like. Typically, alkyl chains of C₁₂-C₁₆ are preferred for lower wash temperatures (e.g., below about 50°C) and C₁₆-C₁₈ alkyl chains are preferred for higher wash temperatures (e.g., about 50°C).

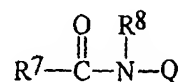
Alkyl alkoxyated sulfate surfactants are another category of preferred anionic surfactant. These surfactants are water soluble salts or acids typically of the formula RO(A)_mSO₃M wherein R is an unsubstituted C₁₀-C₂₄ alkyl or hydroxyalkyl group having a C₁₀-C₂₄ alkyl component, preferably a C₁₂-C₂₀ alkyl or hydroxyalkyl, more preferably C₁₂-C₁₈ alkyl or hydroxyalkyl, A is an ethoxy or propoxy unit, m is greater than zero, typically between about 0.5 and about 6, more preferably between about 0.5 and about 3, and M is hydrogen or a water soluble cation which can be, for example, a metal cation (e.g., sodium, potassium, lithium, calcium, magnesium, etc.), ammonium or substituted-ammonium cation. Alkyl ethoxyated sulfates as well as alkyl propoxyated sulfates are contemplated herein. Specific examples of substituted ammonium cations include methyl-, dimethyl-, trimethyl-ammonium and quaternary ammonium cations, such

as tetramethyl-ammonium, dimethyl piperdinium and cations derived from alkanolamines, e.g., monoethanolamine, diethanolamine, and triethanolamine, and mixtures thereof. Exemplary surfactants are C₁₂-C₁₈ alkyl polyethoxylate (1.0) sulfate, C₁₂-C₁₈ alkyl polyethoxylate (2.25) sulfate, C₁₂-C₁₈ alkyl polyethoxylate (3.0) sulfate, and C₁₂-C₁₈ alkyl polyethoxylate (4.0) sulfate wherein M is conveniently selected from sodium and potassium.

The compositions of the present invention also preferably comprise at least about 0.01%, preferably at least 0.1%, more preferably from about 1% to about 95%, most preferably from about 1% to about 80% by weight, of an nonionic deterative surfactant. Preferred nonionic surfactants such as C₁₂-C₁₈ alkyl ethoxylates ("AE") including the so-called narrow peaked alkyl ethoxylates and C₆-C₁₂ alkyl phenol alkoxylates (especially ethoxylates and mixed ethoxy/propoxy), block alkylene oxide condensate of C₆ to C₁₂ alkyl phenols, alkylene oxide condensates of C₈-C₂₂ alkanols and ethylene oxide/propylene oxide block polymers (Pluronic™-BASF Corp.), as well as semi polar nonionics (e.g., amine oxides and phosphine oxides) can be used in the present compositions. An extensive disclosure of these types of surfactants is found in U.S. Pat. 3,929,678, Laughlin et al., issued December 30, 1975, incorporated herein by reference.

Alkylpolysaccharides such as disclosed in U.S. Pat. 4,565,647 Llenado (incorporated herein by reference) are also preferred nonionic surfactants in the compositions of the invention.

Further preferred nonionic surfactants are the polyhydroxy fatty acid amides having the formula:



wherein R⁷ is C₅-C₃₁ alkyl, preferably straight chain C₇-C₁₉ alkyl or alkenyl, more preferably straight chain C₉-C₁₇ alkyl or alkenyl, most preferably straight chain C₁₁-C₁₅ alkyl or alkenyl, or mixtures thereof; R⁸ is selected from the group consisting of hydrogen, C₁-C₄ alkyl, C₁-C₄ hydroxyalkyl, preferably methyl or ethyl, more preferably methyl. Q is a polyhydroxyalkyl moiety having a linear alkyl chain with at least 3 hydroxyls directly connected to the chain, or an alkoxylated derivative thereof; preferred alkoxy is ethoxy or

propoxy, and mixtures thereof. Preferred Q is derived from a reducing sugar in a reductive amination reaction. More preferably Q is a glycityl moiety. Suitable reducing sugars include glucose, fructose, maltose, lactose, galactose, mannose, and xylose. As raw materials, high dextrose corn syrup, high fructose corn syrup, and high maltose corn syrup can be utilized as well as the individual sugars listed above. These corn syrups may yield a mix of sugar components for Q. It should be understood that it is by no means intended to exclude other suitable raw materials. Q is more preferably selected from the group consisting of $-\text{CH}_2(\text{CHOH})_n\text{CH}_2\text{OH}$, $-\text{CH}(\text{CH}_2\text{OH})(\text{CHOH})_{n-1}\text{CH}_2\text{OH}$, $-\text{CH}_2(\text{CHOH})_2-(\text{CHOR}')(\text{CHOH})\text{CH}_2\text{OH}$, and alkoxylated derivatives thereof, wherein n is an integer from 3 to 5, inclusive, and R' is hydrogen or a cyclic or aliphatic monosaccharide. Most preferred substituents for the Q moiety are glycityls wherein n is 4, particularly $-\text{CH}_2(\text{CHOH})_4\text{CH}_2\text{OH}$.

$\text{R}^7\text{CO-N}<$ can be, for example, cocamide, stearamide, oleamide, lauramide, myristamide, capricamide, palmitamide, tallowamide, etc.

R^8 can be, for example, methyl, ethyl, propyl, isopropyl, butyl, 2-hydroxy ethyl, or 2-hydroxy propyl.

Q can be 1-deoxyglucityl, 2-deoxyfructityl, 1-deoxymaltityl, 1-deoxylactityl, 1-deoxygalactityl, 1-deoxymannityl, 1-deoxymaltotriosityl, etc.

A particularly desirable surfactant of this type for use in the compositions herein is alkyl-N-methyl glucomide, a compound of the above formula wherein R^7 is alkyl (preferably $\text{C}_{11}\text{-C}_{13}$), R^8 is methyl and Q is 1-deoxyglucityl.

Other sugar-derived surfactants include the N-alkoxy polyhydroxy fatty acid amides, such as $\text{C}_{10}\text{-C}_{18}$ N-(3-methoxypropyl) glucamide. The N-propyl through N-hexyl $\text{C}_{12}\text{-C}_{18}$ glucamides can be used for low sudsing. $\text{C}_{10}\text{-C}_{20}$ conventional soaps may also be used. If high sudsing is desired, the branched-chain $\text{C}_{10}\text{-C}_{16}$ soaps may be used.

Optionals

The compositions herein can further comprise a variety of optional ingredients.

A wide variety of other ingredients useful in detergent compositions can be included in the compositions herein, including other active ingredients, carriers, hydrotropes, processing aids, dyes or pigments, solvents for liquid formulations, solid fillers for bar compositions, etc. If high sudsing is desired, suds boosters such as the C₁₀-C₁₆ alkanolamides can be incorporated into the compositions, typically at 1%-10% levels. The C₁₀-C₁₄ monoethanol and diethanol amides illustrate a typical class of such suds boosters. Use of such suds boosters with high sudsing adjunct surfactants such as the amine oxides, betaines and sultaines noted above is also advantageous. If desired, soluble magnesium salts such as MgCl₂, MgSO₄, and the like, can be added at levels of, typically, 0.1%-2%, to provide additional suds and to enhance grease removal performance.

Various deterative ingredients employed in the present compositions optionally can be further stabilized by absorbing said ingredients onto a porous hydrophobic substrate, then coating said substrate with a hydrophobic coating. Preferably, the deterative ingredient is admixed with a surfactant before being absorbed into the porous substrate. In use, the deterative ingredient is released from the substrate into the aqueous washing liquor, where it performs its intended deterative function.

To illustrate this technique in more detail, a porous hydrophobic silica (trademark SIPERNAT D10, DeGussa) is admixed with a proteolytic enzyme solution containing 3%-5% of C₁₃₋₁₅ ethoxylated alcohol (EO 7) nonionic surfactant. Typically, the enzyme/surfactant solution is 2.5 X the weight of silica. The resulting powder is dispersed with stirring in silicone oil (various silicone oil viscosities in the range of 500-12,500 can be used). The resulting silicone oil dispersion is emulsified or otherwise added to the final detergent matrix. By this means, ingredients such as the aforementioned enzymes, bleaches, bleach activators, bleach catalysts, photoactivators, dyes, fluorescers, fabric conditioners and hydrolyzable surfactants can be "protected" for use in detergents, including liquid laundry detergent compositions.

Liquid detergent compositions can contain water and other solvents as carriers. Low molecular weight primary or secondary alcohols exemplified by methanol, ethanol, propanol, and isopropanol are suitable. Monohydric alcohols are preferred for

solubilizing surfactant, but polyols such as those containing from 2 to about 6 carbon atoms and from 2 to about 6 hydroxy groups (e.g., 1,3-propanediol, ethylene glycol, glycerin, and 1,2-propanediol) can also be used. The compositions may contain from 5% to 90%, typically 10% to 50% of such carriers.

The detergent compositions herein will preferably be formulated such that, during use in aqueous cleaning operations, the wash water will have a pH of between about 6.0 and about 11, preferably between about 7.0 and 10.0. Laundry liquid products are typically at pH 7-9. Techniques for controlling pH at recommended usage levels include the use of buffers, alkalis, acids, etc., and are well known to those skilled in the art.

Enzymes

Enzymes can be included in the present detergent compositions for a variety of purposes, including removal of protein-based, carbohydrate-based, or triglyceride-based stains from surfaces such as textiles, for the prevention of refugee dye transfer, for example in laundering, and for fabric restoration. Suitable enzymes include proteases, amylases, lipases, cellulases, peroxidases, and mixtures thereof of any suitable origin, such as vegetable, animal, bacterial, fungal and yeast origin. Preferred selections are influenced by factors such as pH-activity and/or stability optima, thermostability, and stability to active detergents, builders and the like. In this respect bacterial or fungal enzymes are preferred, such as bacterial amylases and proteases, and fungal cellulases.

"Detergent enzyme", as used herein, means any enzyme having a cleaning, stain removing or otherwise beneficial effect in a laundry, hard surface cleaning or personal care detergent composition. Preferred detergent enzymes are hydrolases such as proteases, amylases and lipases. Preferred enzymes for laundry purposes include, but are not limited to, proteases, cellulases, lipases and peroxidases.

Enzymes are normally incorporated into detergent or detergent additive compositions at levels sufficient to provide a "cleaning-effective amount". The term "cleaning effective amount" refers to any amount capable of producing a cleaning, stain removal, soil removal, whitening, deodorizing, or freshness improving effect on substrates such as fabrics. In practical terms for current commercial preparations, typical amounts are up to about 5 mg by weight, more typically 0.01 mg to 3 mg, of active

enzyme per gram of the detergent composition. Stated otherwise, the compositions herein will typically comprise from 0.001% to 5%, preferably 0.01%-1% by weight of a commercial enzyme preparation. Protease enzymes are usually present in such commercial preparations at levels sufficient to provide from 0.005 to 0.1 Anson units (AU) of activity per gram of composition. For certain detergents, it may be desirable to increase the active enzyme content of the commercial preparation in order to minimize the total amount of non-catalytically active materials and thereby improve spotting/filming or other end-results. Higher active levels may also be desirable in highly concentrated detergent formulations.

Amylases suitable herein include, for example, α -amylases described in GB 1,296,839 to Novo; RAPIDASE®, International Bio-Synthetics, Inc. and TERMAMYL®, Novo. FUNGAMYL® from Novo is especially useful. Engineering of enzymes for improved stability, e.g., oxidative stability, is known. See, for example J. Biological Chem., Vol. 260, No. 11, June 1985, pp 6518-6521. Certain preferred embodiments of the present compositions can make use of amylases having improved stability in detergents, especially improved oxidative stability as measured against a reference-point of TERMAMYL® in commercial use in 1993. These preferred amylases herein share the characteristic of being "stability-enhanced" amylases, characterized, at a minimum, by a measurable improvement in one or more of: oxidative stability, e.g., to hydrogen peroxide / tetraacetythylenediamine in buffered solution at pH 9-10; thermal stability, e.g., at common wash temperatures such as about 60°C; or alkaline stability, e.g., at a pH from about 8 to about 11, measured versus the above-identified reference-point amylase. Stability can be measured using any of the art-disclosed technical tests. See, for example, references disclosed in WO 9402597. Stability-enhanced amylases can be obtained from Novo or from Genencor International. One class of highly preferred amylases herein have the commonality of being derived using site-directed mutagenesis from one or more of the *Bacillus* amylases, especially the *Bacillus* α -amylases, regardless of whether one, two or multiple amylase strains are the immediate precursors. Oxidative stability-enhanced amylases vs. the above-identified reference amylase are preferred for use, especially in bleaching, more preferably oxygen bleaching, as distinct

from chlorine bleaching, detergent compositions herein. Such preferred amylases include (a) an amylase according to the hereinbefore incorporated WO 9402597, Novo, Feb. 3, 1994, as further illustrated by a mutant in which substitution is made, using alanine or threonine, preferably threonine, of the methionine residue located in position 197 of the *B.licheniformis* alpha-amylase, known as TERMAMYL®, or the homologous position variation of a similar parent amylase, such as *B. amyloliquefaciens*, *B.subtilis*, or *B.stearothermophilus*; (b) stability-enhanced amylases as described by Genencor International in a paper entitled "Oxidatively Resistant alpha-Amylases" presented at the 207th American Chemical Society National Meeting, March 13-17 1994, by C. Mitchinson. Therein it was noted that bleaches in automatic dishwashing detergents inactivate alpha-amylases but that improved oxidative stability amylases have been made by Genencor from *B.licheniformis* NCIB8061. Methionine (Met) was identified as the most likely residue to be modified. Met was substituted, one at a time, in positions 8, 15, 197, 256, 304, 366 and 438 leading to specific mutants, particularly important being M197L and M197T with the M197T variant being the most stable expressed variant. Stability was measured in CASCADE® and SUNLIGHT®; (c) particularly preferred amylases herein include amylase variants having additional modification in the immediate parent as described in WO 9510603 A and are available from the assignee. Novo, as DURAMYL®. Other particularly preferred oxidative stability enhanced amylase include those described in WO 9418314 to Genencor International and WO 9402597 to Novo. Any other oxidative stability-enhanced amylase can be used, for example as derived by site-directed mutagenesis from known chimeric, hybrid or simple mutant parent forms of available amylases. Other preferred enzyme modifications are accessible. See WO 9509909 A to Novo.

Cellulases usable herein include both bacterial and fungal types, preferably having a pH optimum between 5 and 9.5. U.S. 4,435,307, Barbesgaard et al, March 6, 1984, discloses suitable fungal cellulases from *Humicola insolens* or *Humicola* strain DSM1800 or a cellulase 212-producing fungus belonging to the genus *Aeromonas*, and cellulase extracted from the hepatopancreas of a marine mollusk, *Dolabella Auricula Solander*. Suitable cellulases are also disclosed in GB-A-2.075.028; GB-A-2.095.275

and DE-OS-2.247.832. CAREZYME® (Novo) is especially useful. See also WO 9117243 to Novo.

Suitable lipase enzymes for detergent usage include those produced by microorganisms of the *Pseudomonas* group, such as *Pseudomonas stutzeri* ATCC 19.154, as disclosed in GB 1,372,034. See also lipases in Japanese Patent Application 53,20487, laid open Feb. 24, 1978. This lipase is available from Amano Pharmaceutical Co. Ltd., Nagoya, Japan, under the trade name Lipase P "Amano," or "Amano-P." Other suitable commercial lipases include Amano-CES, lipases ex *Chromobacter viscosum*, e.g. *Chromobacter viscosum* var. *lipolyticum* NRRLB 3673 from Toyo Jozo Co., Tagata, Japan; *Chromobacter viscosum* lipases from U.S. Biochemical Corp., U.S.A. and Disoynt Co., The Netherlands, and lipases ex *Pseudomonas gladioli*. LIPOLASE® enzyme derived from *Humicola lanuginosa* and commercially available from Novo, see also EP 341,947, is a preferred lipase for use herein. Lipase and amylase variants stabilized against peroxidase enzymes are described in WO 9414951 A to Novo. See also WO 9205249 and RD 94359044.

Cutinase enzymes suitable for use herein are described in WO 8809367 A to Genencor.

Suitable examples of proteases are the subtilisins which are obtained from particular strains of *B. subtilis* and *B. licheniformis*. One suitable protease is obtained from a strain of *Bacillus*, having maximum activity throughout the pH range of 8-12, developed and sold as ESPERASE® by Novo Industries A/S of Denmark, hereinafter "Novo". The preparation of this enzyme and analogous enzymes is described in GB 1,243,784 to Novo. Other suitable proteases include ALCALASE® and SAVINASE® from Novo and MAXATASE® from International Bio-Synthetics, Inc., The Netherlands; as well as Protease A as disclosed in EP 130,756 A, January 9, 1985 and Protease B as disclosed in EP 303,761 A, April 28, 1987 and EP 130,756 A, January 9, 1985. See also a high pH protease from *Bacillus* sp. NCIMB 40338 described in WO 9318140 A to Novo. Enzymatic detergents comprising protease, one or more other enzymes, and a reversible protease inhibitor are described in WO 9203529 A to Novo. Other preferred proteases include those of WO 9510591 A to Procter & Gamble. When desired, a

protease having decreased adsorption and increased hydrolysis is available as described in WO 9507791 to Procter & Gamble. A recombinant trypsin-like protease for detergents suitable herein is described in WO 9425583 to Novo.

The preferred liquid laundry detergent compositions according to the present invention further comprise at least 0.001% by weight, of a protease enzyme. However, an effective amount of protease enzyme is sufficient for use in the liquid laundry detergent compositions described herein. The term "an effective amount" refers to any amount capable of producing a cleaning, stain removal, soil removal, whitening, deodorizing, or freshness improving effect on substrates such as fabrics. In practical terms for current commercial preparations, typical amounts are up to about 5 mg by weight, more typically 0.01 mg to 3 mg, of active enzyme per gram of the detergent composition. Stated otherwise, the compositions herein will typically comprise from 0.001% to 5%, preferably 0.01%-1% by weight of a commercial enzyme preparation. The protease enzymes of the present invention are usually present in such commercial preparations at levels sufficient to provide from 0.005 to 0.1 Anson units (AU) of activity per gram of composition.

Preferred liquid laundry detergent compositions of the present invention comprise a protease enzyme, referred to as "Protease D", which is a carbonyl hydrolase variant having an amino acid sequence not found in nature, which is derived from a precursor carbonyl hydrolase by substituting a different amino acid for a plurality of amino acid residues at a position in said carbonyl hydrolase equivalent to position +76, preferably also in combination with one or more amino acid residue positions equivalent to those selected from the group consisting of +99, +101, +103, +104, +107, +123, +27, +105, +109, +126, +128, +135, +156, +166, +195, +197, +204, +206, +210, +216, +217, +218, +222, +260, +265, and/or +274 according to the numbering of *Bacillus amyloliquefaciens* subtilisin, as described in WO 95/10615 published April 20, 1995 by Genencor International.

Useful proteases are also described in PCT publications: WO 95/30010 published November 9, 1995 by The Procter & Gamble Company; WO 95/30011 published

November 9, 1995 by The Procter & Gamble Company; WO 95/29979 published November 9, 1995 by The Procter & Gamble Company.

Preferred proteolytic enzymes are also modified bacterial serine proteases, such as those described in European Patent Application Serial Number 87 303,761.8, filed April 28, 1987 (particularly pages 17, 24 and 98), and which is called herein "Protease B", and in European Patent Application 199,404, Venegas, published October 29, 1986, which refers to a modified bacterial serine proteolytic enzyme which is called "Protease A" herein, Protease A as disclosed in EP 130,756 A, January 9, 1985 and Protease B as disclosed in EP 303,761 A, April 28, 1987 and EP 130,756 A, January 9, 1985.

Peroxidase enzymes may be used in combination with oxygen sources, e.g., percarbonate, perborate, hydrogen peroxide, etc., for "solution bleaching" or prevention of transfer of dyes or pigments removed from substrates during the wash to other substrates present in the wash solution. Known peroxidases include horseradish peroxidase, ligninase, and haloperoxidases such as chloro- or bromo-peroxidase. Peroxidase-containing detergent compositions are disclosed in WO 89099813 A, October 19, 1989 to Novo and WO 8909813 A to Novo.

A range of enzyme materials and means for their incorporation into synthetic detergent compositions is also disclosed in WO 9307263 A and WO 9307260 A to Genencor International, WO 8908694 A to Novo, and U.S. 3,553,139, January 5, 1971 to McCarty et al. Enzymes are further disclosed in U.S. 4,101,457, Place et al, July 18, 1978, and in U.S. 4,507,219, Hughes, March 26, 1985. Enzyme materials useful for liquid detergent formulations, and their incorporation into such formulations, are disclosed in U.S. 4,261,868, Hora et al, April 14, 1981. Enzymes for use in detergents can be stabilized by various techniques. Enzyme stabilization techniques are disclosed and exemplified in U.S. 3,600,319, August 17, 1971, Gedge et al, EP 199,405 and EP 200,586, October 29, 1986, Venegas. Enzyme stabilization systems are also described, for example, in U.S. 3,519,570. A useful *Bacillus*, sp. AC13 giving proteases, xylanases and cellulases, is described in WO 9401532 A to Novo.

Enzyme Stabilizing System

Enzyme-containing, including but not limited to, liquid compositions, herein may comprise from about 0.001% to about 10%, preferably from about 0.005% to about 8%, most preferably from about 0.01% to about 6%, by weight of an enzyme stabilizing system. The enzyme stabilizing system can be any stabilizing system which is compatible with the detergent enzyme. Such a system may be inherently provided by other formulation actives, or be added separately, e.g., by the formulator or by a manufacturer of detergent-ready enzymes. Such stabilizing systems can, for example, comprise calcium ion, boric acid, propylene glycol, short chain carboxylic acids, boronic acids, and mixtures thereof, and are designed to address different stabilization problems depending on the type and physical form of the detergent composition.

One stabilizing approach is the use of water-soluble sources of calcium and/or magnesium ions in the finished compositions which provide such ions to the enzymes. Calcium ions are generally more effective than magnesium ions and are preferred herein if only one type of cation is being used. Typical detergent compositions, especially liquids, will comprise from about 1 to about 30, preferably from about 2 to about 20, more preferably from about 8 to about 12 millimoles of calcium ion per liter of finished detergent composition, though variation is possible depending on factors including the multiplicity, type and levels of enzymes incorporated. Preferably water-soluble calcium or magnesium salts are employed, including for example calcium chloride, calcium hydroxide, calcium formate, calcium malate, calcium maleate, calcium hydroxide and calcium acetate; more generally, calcium sulfate or magnesium salts corresponding to the exemplified calcium salts may be used. Further increased levels of Calcium and/or Magnesium may of course be useful, for example for promoting the grease-cutting action of certain types of surfactant.

Another stabilizing approach is by use of borate species. See Severson, U.S. 4,537,706. Borate stabilizers, when used, may be at levels of up to 10% or more of the composition though more typically, levels of up to about 3% by weight of boric acid or other borate compounds such as borax or orthoborate are suitable for liquid detergent use. Substituted boric acids such as phenylboronic acid, butaneboronic acid, p-bromophenylboronic acid or the like can be used in place of boric acid and reduced

levels of total boron in detergent compositions may be possible though the use of such substituted boron derivatives.

Stabilizing systems of certain cleaning compositions may further comprise from 0 to about 10%, preferably from about 0.01% to about 6% by weight, of chlorine bleach scavengers, added to prevent chlorine bleach species present in many water supplies from attacking and inactivating the enzymes, especially under alkaline conditions. While chlorine levels in water may be small, typically in the range from about 0.5 ppm to about 1.75 ppm, the available chlorine in the total volume of water that comes in contact with the enzyme, for example during fabric-washing, can be relatively large; accordingly, enzyme stability to chlorine in-use is sometimes problematic. Since perborate or percarbonate, which have the ability to react with chlorine bleach, may present in certain of the instant compositions in amounts accounted for separately from the stabilizing system, the use of additional stabilizers against chlorine, may, most generally, not be essential, though improved results may be obtainable from their use. Suitable chlorine scavenger anions are widely known and readily available, and, if used, can be salts containing ammonium cations with sulfite, bisulfite, thiosulfite, thiosulfate, iodide, etc. Antioxidants such as carbamate, ascorbate, etc., organic amines such as ethylenediaminetetracetic acid (EDTA) or alkali metal salt thereof, monoethanolamine (MEA), and mixtures thereof can likewise be used. Likewise, special enzyme inhibition systems can be incorporated such that different enzymes have maximum compatibility. Other conventional scavengers such as bisulfate, nitrate, chloride, sources of hydrogen peroxide such as sodium perborate tetrahydrate, sodium perborate monohydrate and sodium percarbonate, as well as phosphate, condensed phosphate, acetate, benzoate, citrate, formate, lactate, malate, tartrate, salicylate, etc., and mixtures thereof can be used if desired. In general, since the chlorine scavenger function can be performed by ingredients separately listed under better recognized functions, (e.g., hydrogen peroxide sources), there is no absolute requirement to add a separate chlorine scavenger unless a compound performing that function to the desired extent is absent from an enzyme-containing embodiment of the invention; even then, the scavenger is added only for optimum results. Moreover, the formulator will exercise a chemist's normal skill in

avoiding the use of any enzyme scavenger or stabilizer which is majorly incompatible, as formulated, with other reactive ingredients, if used. In relation to the use of ammonium salts, such salts can be simply admixed with the detergent composition but are prone to adsorb water and/or liberate ammonia during storage. Accordingly, such materials, if present, are desirably protected in a particle such as that described in US 4,652,392, Baginski et al.

Builders

Detergent builders can optionally be included in the compositions herein to assist in controlling mineral hardness. Inorganic as well as organic builders can be used. Builders are typically used in fabric laundering compositions to assist in the removal of particulate soils.

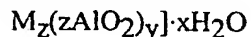
The level of builder can vary widely depending upon the end use of the composition and its desired physical form. When present, the compositions will typically comprise at least about 1% builder. Liquid formulations typically comprise from about 5% to about 50%, more typically about 5% to about 30%, by weight, of detergent builder. Lower or higher levels of builder, however, are not meant to be excluded.

Inorganic or P-containing detergent builders include, but are not limited to, the alkali metal, ammonium and alkanolammonium salts of polyphosphates (exemplified by the tripolyphosphates, pyrophosphates, and glassy polymeric meta-phosphates), phosphonates, phytic acid, silicates, carbonates (including bicarbonates and sesquicarbonates), sulphates, and aluminosilicates. However, non-phosphate builders are required in some locales. Importantly, the compositions herein function surprisingly well even in the presence of the so-called "weak" builders (as compared with phosphates) such as citrate, or in the so-called "underbuilt" situation that may occur with zeolite or layered silicate builders.

Examples of silicate builders are the alkali metal silicates, particularly those having a $\text{SiO}_2:\text{Na}_2\text{O}$ ratio in the range 1.6:1 to 3.2:1 and layered silicates, such as the layered sodium silicates described in U.S. Patent 4,664,839.

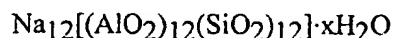
Examples of carbonate builders are the alkaline earth and alkali metal carbonates as disclosed in German Patent Application No. 2,321,001 published on November 15, 1973.

Aluminosilicate builders are useful in the present invention. Aluminosilicate builders include those having the empirical formula:



wherein z and y are integers of at least 6, the molar ratio of z to y is in the range from 1.0 to about 0.5, and x is an integer from about 15 to about 264.

Useful aluminosilicate ion exchange materials are commercially available. These aluminosilicates can be crystalline or amorphous in structure and can be naturally-occurring aluminosilicates or synthetically derived. A method for producing aluminosilicate ion exchange materials is disclosed in U.S. Patent 3,985,669, Krummel, et al, issued October 12, 1976. Preferred synthetic crystalline aluminosilicate ion exchange materials useful herein are available under the designations Zeolite A, Zeolite P (B), Zeolite MAP and Zeolite X. In an especially preferred embodiment, the crystalline aluminosilicate ion exchange material has the formula:



wherein x is from about 20 to about 30, especially about 27. This material is known as Zeolite A. Dehydrated zeolites (x = 0 - 10) may also be used herein. Preferably, the aluminosilicate has a particle size of about 0.1-10 microns in diameter.

Organic detergent builders suitable for the purposes of the present invention include, but are not restricted to, a wide variety of polycarboxylate compounds. As used herein, "polycarboxylate" refers to compounds having a plurality of carboxylate groups, preferably at least 3 carboxylates. Polycarboxylate builder can generally be added to the composition in acid form, but can also be added in the form of a neutralized salt. When utilized in salt form, alkali metals, such as sodium, potassium, and lithium, or alkanolammonium salts are preferred.

Included among the polycarboxylate builders are a variety of categories of useful materials. One important category of polycarboxylate builders encompasses the ether polycarboxylates, including oxydisuccinate, as disclosed in Berg, U.S. Patent 3,128,287,

issued April 7, 1964, and Lamberti et al, U.S. Patent 3,635,830, issued January 18, 1972. See also "TMS/TDS" builders of U.S. Patent 4,663,071, issued to Bush et al, on May 5, 1987. Suitable ether polycarboxylates also include cyclic compounds, particularly alicyclic compounds, such as those described in U.S. Patents 3,923,679; 3,835,163; 4,158,635; 4,120,874 and 4,102,903.

Other useful detergency builders include the ether hydroxypolycarboxylates, copolymers of maleic anhydride with ethylene or vinyl methyl ether, 1, 3, 5-trihydroxy benzene-2, 4, 6-trisulphonic acid, and carboxymethyloxysuccinic acid, the various alkali metal, ammonium and substituted ammonium salts of polyacetic acids such as ethylenediamine tetraacetic acid and nitrilotriacetic acid, as well as polycarboxylates such as mellitic acid, succinic acid, oxydisuccinic acid, polymaleic acid, benzene 1,3,5-tricarboxylic acid, carboxymethyloxysuccinic acid, and soluble salts thereof.

Citrate builders, e.g., citric acid and soluble salts thereof (particularly sodium salt), are polycarboxylate builders of particular importance for heavy duty liquid detergent formulations due to their availability from renewable resources and their biodegradability. Oxydisuccinates are also especially useful in such compositions and combinations.

Also suitable in the detergent compositions of the present invention are the 3,3-dicarboxy-4-oxa-1,6-hexanedioates and the related compounds disclosed in U.S. Patent 4,566,984, Bush, issued January 28, 1986. Useful succinic acid builders include the C₅-C₂₀ alkyl and alkenyl succinic acids and salts thereof. A particularly preferred compound of this type is dodecenylsuccinic acid. Specific examples of succinate builders include: laurylsuccinate, myristylsuccinate, palmitylsuccinate, 2-dodecenylsuccinate (preferred), 2-pentadecenylsuccinate, and the like. Laurylsuccinates are the preferred builders of this group, and are described in European Patent Application 86200690.5/0,200,263, published November 5, 1986.

Other suitable polycarboxylates are disclosed in U.S. Patent 4,144,226, Crutchfield et al, issued March 13, 1979 and in U.S. Patent 3,308,067, Diehl, issued March 7, 1967. See also Diehl U.S. Patent 3,723,322.

Fatty acids, e.g., C₁₂-C₁₈ monocarboxylic acids, can also be incorporated into the compositions alone, or in combination with the aforesaid builders, especially citrate and/or the succinate builders, to provide additional builder activity. Such use of fatty acids will generally result in a diminution of sudsing, which should be taken into account by the formulator.

In situations where phosphorus-based builders can be used, and especially in the formulation of bars used for hand-laundrying operations, the various alkali metal phosphates such as the well-known sodium tripolyphosphates, sodium pyrophosphate and sodium orthophosphate can be used. Phosphonate builders (see, for example, U.S. Patents 3,159,581; 3,213,030; 3,422,021; 3,400,148 and 3,422,137) can also be used.

Chelating Agents

The detergent compositions herein may also optionally contain one or more iron and/or manganese chelating agents. Such chelating agents can be selected from the group consisting of amino carboxylates, amino phosphonates, polyfunctionally-substituted aromatic chelating agents and mixtures therein, all as hereinafter defined. Without intending to be bound by theory, it is believed that the benefit of these materials is due in part to their exceptional ability to remove iron and manganese ions from washing solutions by formation of soluble chelates.

Amino carboxylates useful as optional chelating agents include ethylenediaminetetracetates, N-hydroxyethylethylenediaminetriacetates, nitrilotriacetates, ethylenediamine tetrapropionates, triethylenetetraaminehexacetates, diethylenetriaminepentaacetates, and ethanoldiglycines, alkali metal, ammonium, and substituted ammonium salts therein and mixtures therein.

Amino phosphonates are also suitable for use as chelating agents in the compositions of the invention and include ethylenediaminetetrakis (methylenephosphonates) as DEQUEST. Preferred, these amino phosphonates to not contain alkyl or alkenyl groups with more than about 6 carbon atoms.

Polyfunctionally-substituted aromatic chelating agents are also useful in the compositions herein. See U.S. Patent 3,812,044, issued May 21, 1974, to Connor et al.

Preferred compounds of this type in acid form are dihydroxydisulfobenzenes such as 1,2-dihydroxy-3,5-disulfobenzene.

A preferred biodegradable chelator for use herein is ethylenediamine disuccinate ("EDDS"), especially the [S,S] isomer as described in U.S. Patent 4,704,233, November 3, 1987, to Hartman and Perkins.

If utilized, these chelating agents will generally comprise from about 0.1% to about 10% by weight of the detergent compositions herein. More preferably, if utilized, the chelating agents will comprise from about 0.1% to about 3.0% by weight of such compositions.

Clay Soil Removal/Anti-redeposition Agents

The compositions of the present invention can also optionally contain water-soluble ethoxylated amines having clay soil removal and antiredeposition properties. Granular detergent compositions which contain these compounds typically contain from about 0.01% to about 10.0% by weight of the water-soluble ethoxylates amines; liquid detergent compositions typically contain about 0.01% to about 5%.

The most preferred soil release and anti-redeposition agent is ethoxylated tetraethylenepentamine. Exemplary ethoxylated amines are further described in U.S. Patent 4,597,898, VanderMeer, issued July 1, 1986. Another group of preferred clay soil removal-antiredeposition agents are the cationic compounds disclosed in European Patent Application 111,965, Oh and Gosselink, published June 27, 1984. Other clay soil removal/antiredeposition agents which can be used include the ethoxylated amine polymers disclosed in European Patent Application 111,984, Gosselink, published June 27, 1984; the zwitterionic polymers disclosed in European Patent Application 112,592, Gosselink, published July 4, 1984; and the amine oxides disclosed in U.S. Patent 4,548,744, Connor, issued October 22, 1985. Other clay soil removal and/or antiredeposition agents known in the art can also be utilized in the compositions herein. Another type of preferred antiredeposition agent includes the carboxy methyl cellulose (CMC) materials. These materials are well known in the art.

Polymeric Dispersing Agents

Polymeric dispersing agents can advantageously be utilized at levels from about 0.1% to about 7%, by weight, in the compositions herein, especially in the presence of zeolite and/or layered silicate builders. Suitable polymeric dispersing agents include polymeric polycarboxylates and polyethylene glycols, although others known in the art can also be used. It is believed, though it is not intended to be limited by theory, that polymeric dispersing agents enhance overall detergent builder performance, when used in combination with other builders (including lower molecular weight polycarboxylates) by crystal growth inhibition, particulate soil release peptization, and anti-redeposition.

Polymeric polycarboxylate materials can be prepared by polymerizing or copolymerizing suitable unsaturated monomers, preferably in their acid form. Unsaturated monomeric acids that can be polymerized to form suitable polymeric polycarboxylates include acrylic acid, maleic acid (or maleic anhydride), fumaric acid, itaconic acid, aconitic acid, mesaconic acid, citraconic acid and methylenemalononic acid. The presence in the polymeric polycarboxylates herein or monomeric segments, containing no carboxylate radicals such as vinylmethyl ether, styrene, ethylene, etc. is suitable provided that such segments do not constitute more than about 40% by weight.

Particularly suitable polymeric polycarboxylates can be derived from acrylic acid. Such acrylic acid-based polymers which are useful herein are the water-soluble salts of polymerized acrylic acid. The average molecular weight of such polymers in the acid form preferably ranges from about 2,000 to 10,000, more preferably from about 4,000 to 7,000 and most preferably from about 4,000 to 5,000. Water-soluble salts of such acrylic acid polymers can include, for example, the alkali metal, ammonium and substituted ammonium salts. Soluble polymers of this type are known materials. Use of polyacrylates of this type in detergent compositions has been disclosed, for example, in Diehl, U.S. Patent 3,308,067, issued march 7, 1967.

Acrylic/maleic-based copolymers may also be used as a preferred component of the dispersing/anti-redeposition agent. Such materials include the water-soluble salts of copolymers of acrylic acid and maleic acid. The average molecular weight of such copolymers in the acid form preferably ranges from about 2,000 to 100,000, more preferably from about 5,000 to 75,000, most preferably from about 7,000 to 65,000. The

ratio of acrylate to maleate segments in such copolymers will generally range from about 30:1 to about 1:1, more preferably from about 10:1 to 2:1. Water-soluble salts of such acrylic acid/maleic acid copolymers can include, for example, the alkali metal, ammonium and substituted ammonium salts. Soluble acrylate/maleate copolymers of this type are known materials which are described in European Patent Application No. 66915, published December 15, 1982, as well as in EP 193,360, published September 3, 1986, which also describes such polymers comprising hydroxypropylacrylate. Still other useful dispersing agents include the maleic/acrylic/vinyl alcohol terpolymers. Such materials are also disclosed in EP 193,360, including, for example, the 45/45/10 terpolymer of acrylic/maleic/vinyl alcohol.

Another polymeric material which can be included is polyethylene glycol (PEG). PEG can exhibit dispersing agent performance as well as act as a clay soil removal-antiredeposition agent. Typical molecular weight ranges for these purposes range from about 500 to about 100,000, preferably from about 1,000 to about 50,000, more preferably from about 1,500 to about 10,000.

Polyaspartate and polyglutamate dispersing agents may also be used, especially in conjunction with zeolite builders. Dispersing agents such as polyaspartate preferably have a molecular weight (avg.) of about 10,000.

Brightener

Any optical brighteners or other brightening or whitening agents known in the art can be incorporated at levels typically from about 0.05% to about 1.2%, by weight, into the detergent compositions herein. Commercial optical brighteners which may be useful in the present invention can be classified into subgroups, which include, but are not necessarily limited to, derivatives of stilbene, pyrazoline, coumarin, carboxylic acid, methinecyanines, dibenzothiphen-5,5-dioxide, azoles, 5- and 6-membered-ring heterocycles, and other miscellaneous agents. Examples of such brighteners are disclosed in "The Production and Application of Fluorescent Brightening Agents", M. Zahradnik, Published by John Wiley & Sons, New York (1982).

Specific examples of optical brighteners which are useful in the present compositions are those identified in U.S. Patent 4,790,856, issued to Wixon on

December 13, 1988. These brighteners include the PHORWHITE series of brighteners from Verona. Other brighteners disclosed in this reference include: Tinopal UNPA, Tinopal CBS and Tinopal 5BM; available from Ciba-Geigy; Artic White CC and Artic White CWD, available from Hilton-Davis, located in Italy; the 2-(4-styryl-phenyl)-2H-naphthol[1,2-d]triazoles; 4,4'-bis-(1,2,3-triazol-2-yl)-stilbenes; 4,4'-bis(styryl)bisphenyls; and the aminocoumarins. Specific examples of these brighteners include 4-methyl-7-diethyl-amino coumarin; 1,2-bis-(benzimidazol-2-yl)ethylene; 1,3-diphenyl-phrazolines; 2,5-bis(benzoxazol-2-yl)thiophene; 2-styryl-naphth-[1,2-d]oxazole; and 2-(stilbene-4-yl)-2H-naphtho-[1,2-d]triazole. See also U.S. Patent 3,646,015, issued February 29, 1972 to Hamilton. Anionic brighteners are preferred herein.

Suds Suppressors

Compounds for reducing or suppressing the formation of suds can be incorporated into the compositions of the present invention. Suds suppression can be of particular importance in the so-called "high concentration cleaning process" as described in U.S. 4,489,455 and 4,489,574 and in front-loading European-style washing machines.

A wide variety of materials may be used as suds suppressors, and suds suppressors are well known to those skilled in the art. See, for example, Kirk Othmer Encyclopedia of Chemical Technology, Third Edition, Volume 7, pages 430-447 (John Wiley & Sons, Inc., 1979). One category of suds suppressor of particular interest encompasses monocarboxylic fatty acid and soluble salts therein. See U.S. Patent 2,954,347, issued September 27, 1960 to Wayne St. John. The monocarboxylic fatty acids and salts thereof used as suds suppressor typically have hydrocarbyl chains of 10 to about 24 carbon atoms, preferably 12 to 18 carbon atoms. Suitable salts include the alkali metal salts such as sodium, potassium, and lithium salts, and ammonium and alkanolammonium salts.

The detergent compositions herein may also contain non-surfactant suds suppressors. These include, for example: high molecular weight hydrocarbons such as paraffin, fatty acid esters (e.g., fatty acid triglycerides), fatty acid esters of monovalent alcohols, aliphatic C₁₈-C₄₀ ketones (e.g., stearone), etc. Other suds inhibitors include N-alkylated amino triazines such as tri- to hexa-alkylmelamines or di- to tetra-

alkyldiamine chlortriazines formed as products of cyanuric chloride with two or three moles of a primary or secondary amine containing 1 to 24 carbon atoms, propylene oxide, and monostearyl phosphates such as monostearyl alcohol phosphate ester and monostearyl di-alkali metal (e.g., K, Na, and Li) phosphates and phosphate esters. The hydrocarbons such as paraffin and haloparaffin can be utilized in liquid form. The liquid hydrocarbons will be liquid at room temperature and atmospheric pressure, and will have a pour point in the range of about -40°C and about 50°C, and a minimum boiling point not less than about 110°C (atmospheric pressure). It is also known to utilize waxy hydrocarbons, preferably having a melting point below about 100°C. The hydrocarbons constitute a preferred category of suds suppressor for detergent compositions. Hydrocarbon suds suppressors are described, for example, in U.S. Patent 4,265,779, issued May 5, 1981 to Gandolfo et al. The hydrocarbons, thus, include aliphatic, alicyclic, aromatic, and heterocyclic saturated or unsaturated hydrocarbons having from about 12 to about 70 carbon atoms. The term "paraffin," as used in this suds suppressor discussion, is intended to include mixtures of true paraffins and cyclic hydrocarbons.

The preferred category of non-surfactant suds suppressors comprises silicone suds suppressors. This category includes the use of polyorganosiloxane oils, such as polydimethylsiloxane, dispersions or emulsions of polyorganosiloxane oils or resins, and combinations of polyorganosiloxane with silica particles wherein the polyorganosiloxane is chemisorbed or fused onto the silica. Silicone suds suppressors are well known in the art and are, for example, disclosed in U.S. Patent 4,265,779, issued May 5, 1981 to Gandolfo et al and European Patent Application No. 89307851.9, published February 7, 1990, by Starch, M. S.

Other silicone suds suppressors are disclosed in U.S. Patent 3,455,839 which relates to compositions and processes for defoaming aqueous solutions by incorporating therein small amounts of polydimethylsiloxane fluids.

Mixtures of silicone and silanated silica are described, for instance, in German Patent Application DOS 2,124,526. Silicone defoamers and suds controlling agents in granular detergent compositions are disclosed in U.S. Patent 3,933,672, Bartolotta et al, and in U.S. Patent 4,652,392, Baginski et al, issued March 24, 1987.

An exemplary silicone based suds suppressor for use herein is a suds suppressing amount of a suds controlling agent consisting essentially of:

- (i) polydimethylsiloxane fluid having a viscosity of from about 20 cs. to about 1,500 cs. at 25°C;
- (ii) from about 5 to about 50 parts per 100 parts by weight of (i) of siloxane resin composed of $(\text{CH}_3)_3\text{SiO}_{1/2}$ units of SiO_2 units in a ratio of from $(\text{CH}_3)_3\text{SiO}_{1/2}$ units and to SiO_2 units of from about 0.6:1 to about 1.2:1; and
- (iii) from about 1 to about 20 parts per 100 parts by weight of (i) of a solid silica gel.

In the preferred silicone suds suppressor used herein, the solvent for a continuous phase is made up of certain polyethylene glycols or polyethylene-polypropylene glycol copolymers or mixtures thereof (preferred), or polypropylene glycol. The primary silicone suds suppressor is branched/crosslinked and preferably not linear.

To illustrate this point further, typical liquid laundry detergent compositions with controlled suds will optionally comprise from about 0.001 to about 1, preferably from about 0.01 to about 0.7, most preferably from about 0.05 to about 0.5, weight % of said silicone suds suppressor, which comprises (1) a nonaqueous emulsion of a primary antifoam agent which is a mixture of (a) a polyorganosiloxane, (b) a resinous siloxane or a silicone resin-producing silicone compound, (c) a finely divided filler material, and (d) a catalyst to promote the reaction of mixture components (a), (b) and (c), to form silanolates; (2) at least one nonionic silicone surfactant; and (3) polyethylene glycol or a copolymer of polyethylene-polypropylene glycol having a solubility in water at room temperature of more than about 2 weight %; and without polypropylene glycol. Similar amounts can be used in granular compositions, gels, etc. See also U.S. Patents 4,978,471, Starch, issued December 18, 1990, and 4,983,316, Starch, issued January 8, 1991, 5,288,431, Huber et al., issued February 22, 1994, and U.S. Patents 4,639,489 and 4,749,740, Aizawa et al at column 1, line 46 through column 4, line 35.

The silicone suds suppressor herein preferably comprises polyethylene glycol and a copolymer of polyethylene glycol/polypropylene glycol, all having an average

molecular weight of less than about 1,000, preferably between about 100 and 800. The polyethylene glycol and polyethylene/polypropylene copolymers herein have a solubility in water at room temperature of more than about 2 weight %, preferably more than about 5 weight %.

The preferred solvent herein is polyethylene glycol having an average molecular weight of less than about 1,000, more preferably between about 100 and 800, most preferably between 200 and 400, and a copolymer of polyethylene glycol/polypropylene glycol, preferably PPG 200/PEG 300. Preferred is a weight ratio of between about 1:1 and 1:10, most preferably between 1:3 and 1:6, of polyethylene glycol:copolymer of polyethylene-polypropylene glycol.

The preferred silicone suds suppressors used herein do not contain polypropylene glycol, particularly of 4,000 molecular weight. They also preferably do not contain block copolymers of ethylene oxide and propylene oxide, like PLURONIC L101.

Other suds suppressors useful herein comprise the secondary alcohols (e.g., 2-alkyl alkanols) and mixtures of such alcohols with silicone oils, such as the silicones disclosed in U.S. 4,798,679, 4,075,118 and EP 150,872. The secondary alcohols include the C₆-C₁₆ alkyl alcohols having a C₁-C₁₆ chain. A preferred alcohol is 2-butyl octanol, which is available from Condea under the trademark ISOFOL 12. Mixtures of secondary alcohols are available under the trademark ISALCHEM 123 from Enichem. Mixed suds suppressors typically comprise mixtures of alcohol + silicone at a weight ratio of 1:5 to 5:1.

For any detergent compositions to be used in automatic laundry washing machines, suds should not form to the extent that they overflow the washing machine. Suds suppressors, when utilized, are preferably present in a "suds suppressing amount." By "suds suppressing amount" is meant that the formulator of the composition can select an amount of this suds controlling agent that will sufficiently control the suds to result in a low-sudsing laundry detergent for use in automatic laundry washing machines.

The compositions herein will generally comprise from 0% to about 5% of suds suppressor. When utilized as suds suppressors, monocarboxylic fatty acids, and salts therein, will be present typically in amounts up to about 5%, by weight, of the detergent

composition. Preferably, from about 0.5% to about 3% of fatty monocarboxylate suds suppressor is utilized. Silicone suds suppressors are typically utilized in amounts up to about 2.0%, by weight, of the detergent composition, although higher amounts may be used. This upper limit is practical in nature, due primarily to concern with keeping costs minimized and effectiveness of lower amounts for effectively controlling sudsing. Preferably from about 0.01% to about 1% of silicone suds suppressor is used, more preferably from about 0.25% to about 0.5%. As used herein, these weight percentage values include any silica that may be utilized in combination with polyorganosiloxane, as well as any adjunct materials that may be utilized. Monostearyl phosphate suds suppressors are generally utilized in amounts ranging from about 0.1% to about 2%, by weight, of the composition. Hydrocarbon suds suppressors are typically utilized in amounts ranging from about 0.01% to about 5.0%, although higher levels can be used. The alcohol suds suppressors are typically used at 0.2%-3% by weight of the finished compositions.

Fabric Softeners

Various through-the-wash fabric softeners, especially the impalpable smectite clays of U.S. Patent 4,062,647, Storm and Nirschl, issued December 13, 1977, as well as other softener clays known in the art, can optionally be used typically at levels of from about 0.5% to about 10% by weight in the present compositions to provide fabric softener benefits concurrently with fabric cleaning. Clay softeners can be used in combination with amine and cationic softeners as disclosed, for example, in U.S. Patent 4,375,416, Crisp et al, March 1, 1983 and U.S. Patent 4,291,071, Harris et al, issued September 22, 1981.

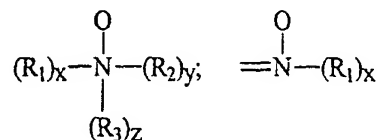
Dye Transfer Inhibiting Agents

The compositions of the present invention may also include one or more materials effective for inhibiting the transfer of dyes from one fabric to another during the cleaning process. Generally, such dye transfer inhibiting agents include polyvinyl pyrrolidone polymers, polyamine N-oxide polymers, copolymers of N-vinylpyrrolidone and N-vinylimidazole, manganese phthalocyanine, peroxidases, and mixtures thereof. If used, these agents typically comprise from about 0.01% to about 10% by weight of the

composition, preferably from about 0.01% to about 5%, and more preferably from about 0.05% to about 2%.

More specifically, the polyamine N-oxide polymers preferred for use herein contain units having the following structural formula: $R-A_x-P$; wherein P is a polymerizable unit to which an N-O group can be attached or the N-O group can form part of the polymerizable unit or the N-O group can be attached to both units; A is one of the following structures: $-NC(O)-$, $-C(O)O-$, $-S-$, $-O-$, $-N=$; x is 0 or 1; and R is aliphatic, ethoxylated aliphatics, aromatics, heterocyclic or alicyclic groups or any combination thereof to which the nitrogen of the N-O group can be attached or the N-O group is part of these groups. Preferred polyamine N-oxides are those wherein R is a heterocyclic group such as pyridine, pyrrole, imidazole, pyrrolidine, piperidine and derivatives thereof.

The N-O group can be represented by the following general structures:



wherein R_1 , R_2 , R_3 are aliphatic, aromatic, heterocyclic or alicyclic groups or combinations thereof; x, y and z are 0 or 1; and the nitrogen of the N-O group can be attached or form part of any of the aforementioned groups. The amine oxide unit of the polyamine N-oxides has a $pK_a < 10$, preferably $pK_a < 7$, more preferred $pK_a < 6$.

Any polymer backbone can be used as long as the amine oxide polymer formed is water-soluble and has dye transfer inhibiting properties. Examples of suitable polymeric backbones are polyvinyls, polyalkylenes, polyesters, polyethers, polyamide, polyimides, polyacrylates and mixtures thereof. These polymers include random or block copolymers where one monomer type is an amine N-oxide and the other monomer type is an N-oxide. The amine N-oxide polymers typically have a ratio of amine to the amine N-oxide of 10:1 to 1:1,000,000. However, the number of amine oxide groups present in the polyamine oxide polymer can be varied by appropriate copolymerization or by an appropriate degree of N-oxidation. The polyamine oxides can be obtained in almost any degree of polymerization. Typically, the average molecular weight is within the range of 500 to

1,000,000; more preferred 1,000 to 500,000; most preferred 5,000 to 100,000. This preferred class of materials can be referred to as "PVNO".

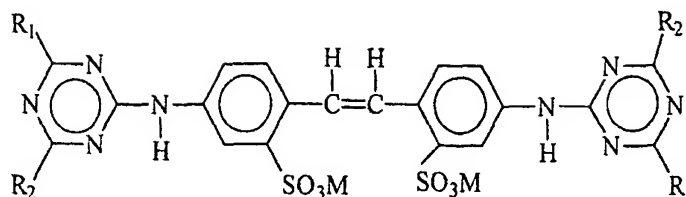
The most preferred polyamine N-oxide useful in the detergent compositions herein is poly(4-vinylpyridine-N-oxide) which as an average molecular weight of about 50,000 and an amine to amine N-oxide ratio of about 1:4.

Copolymers of N-vinylpyrrolidone and N-vinylimidazole polymers (referred to as a class as "PVPVI") are also preferred for use herein. Preferably the PVPVI has an average molecular weight range from 5,000 to 1,000,000, more preferably from 5,000 to 200,000, and most preferably from 10,000 to 20,000. (The average molecular weight range is determined by light scattering as described in Barth, et al., Chemical Analysis, Vol 113. "Modern Methods of Polymer Characterization", the disclosures of which are incorporated herein by reference.) The PVPVI copolymers typically have a molar ratio of N-vinylimidazole to N-vinylpyrrolidone from 1:1 to 0.2:1, more preferably from 0.8:1 to 0.3:1, most preferably from 0.6:1 to 0.4:1. These copolymers can be either linear or branched.

The present invention compositions also may employ a polyvinylpyrrolidone ("PVP") having an average molecular weight of from about 5,000 to about 400,000, preferably from about 5,000 to about 200,000, and more preferably from about 5,000 to about 50,000. PVP's are known to persons skilled in the detergent field; see, for example, EP-A-262,897 and EP-A-256,696, incorporated herein by reference. Compositions containing PVP can also contain polyethylene glycol ("PEG") having an average molecular weight from about 500 to about 100,000, preferably from about 1,000 to about 10,000. Preferably, the ratio of PEG to PVP on a ppm basis delivered in wash solutions is from about 2:1 to about 50:1, and more preferably from about 3:1 to about 10:1.

The detergent compositions herein may also optionally contain from about 0.005% to 5% by weight of certain types of hydrophilic optical brighteners which also provide a dye transfer inhibition action. If used, the compositions herein will preferably comprise from about 0.01% to 1% by weight of such optical brighteners.

The hydrophilic optical brighteners useful in the present invention are those having the structural formula:



wherein R_1 is selected from anilino, N-2-bis-hydroxyethyl and NH-2-hydroxyethyl; R_2 is selected from N-2-bis-hydroxyethyl, N-2-hydroxyethyl-N-methylamino, morphilino, chloro and amino; and M is a salt-forming cation such as sodium or potassium.

When in the above formula, R_1 is anilino, R_2 is N-2-bis-hydroxyethyl and M is a cation such as sodium, the brightener is 4,4'-bis[(4-anilino-6-(N-2-bis-hydroxyethyl)-s-triazine-2-yl)amino]-2,2'-stilbenedisulfonic acid and disodium salt. This particular brightener species is commercially marketed under the tradename Tinopal-UNPA-GX by Ciba-Geigy Corporation. Tinopal-UNPA-GX is the preferred hydrophilic optical brightener useful in the detergent compositions herein.

When in the above formula, R_1 is anilino, R_2 is N-2-hydroxyethyl-N-2-methylamino and M is a cation such as sodium, the brightener is 4,4'-bis[(4-anilino-6-(N-2-hydroxyethyl-N-methylamino)-s-triazine-2-yl)amino]2,2'-stilbenedisulfonic acid disodium salt. This particular brightener species is commercially marketed under the tradename Tinopal 5BM-GX by Ciba-Geigy Corporation.

When in the above formula, R_1 is anilino, R_2 is morphilino and M is a cation such as sodium, the brightener is 4,4'-bis[(4-anilino-6-morphilino-s-triazine-2-yl)amino]2,2'-stilbenedisulfonic acid, sodium salt. This particular brightener species is commercially marketed under the tradename Tinopal AMS-GX by Ciba Geigy Corporation.

The specific optical brightener species selected for use in the present invention provide especially effective dye transfer inhibition performance benefits when used in combination with the selected polymeric dye transfer inhibiting agents hereinbefore described. The combination of such selected polymeric materials (e.g., PVNO and/or PVPVI) with such selected optical brighteners (e.g., Tinopal UNPA-GX, Tinopal 5BM-GX and/or Tinopal AMS-GX) provides significantly better dye transfer inhibition in aqueous wash solutions than does either of these two detergent composition components

when used alone. Without being bound by theory, it is believed that such brighteners work this way because they have high affinity for fabrics in the wash solution and therefore deposit relatively quick on these fabrics. The extent to which brighteners deposit on fabrics in the wash solution can be defined by a parameter called the "exhaustion coefficient". The exhaustion coefficient is in general as the ratio of a) the brightener material deposited on fabric to b) the initial brightener concentration in the wash liquor. Brighteners with relatively high exhaustion coefficients are the most suitable for inhibiting dye transfer in the context of the present invention.

Of course, it will be appreciated that other, conventional optical brightener types of compounds can optionally be used in the present compositions to provide conventional fabric "brightness" benefits, rather than a true dye transfer inhibiting effect. Such usage is conventional and well-known to detergent formulations.

Preparation of polyamines

EXAMPLE 1

Ethoxylation of poly(ethyleneimine) with average molecular weight of 1,800 - To a 250ml 3-neck round bottom flask equipped with a Claisen head, thermometer connected to a temperature controller (Therm-O-Watch™, I²R), sparging tube, and mechanical stirrer is added poly(ethyleneimine) MW 1800 (Polysciences, 50.0g, 0.028 mole). Ethylene oxide gas (Liquid Carbonics) is added via the sparging tube under argon at approximately 140°C with very rapid stirring until a weight gain of 52g (corresponding to 1.2 ethoxy units) is obtained. A 50g portion of this yellow gel-like material is saved. To the remaining material is added potassium hydroxide pellets (Baker, 0.30g, 0.0053 mol). after the potassium hydroxide dissolves, ethylene oxide is added as described above until a weight gain of 60g (corresponding to a total of 4.2 ethoxy units) is obtained. A 53g portion of this brown viscous liquid is saved. Ethylene oxide is added to the remaining material as described above until a weight gain of 35.9g (corresponding to a total of 7.1 ethoxy units) is obtained to afford 94.9g of dark brown

liquid. The potassium hydroxide in the latter two samples is neutralized by adding the theoretical amounts of methanesulfonic acid.

EXAMPLE 2

Quaternization of PEI 1800 E₇

To a 500 mL Erlenmeyer flask equipped with a magnetic stirring bar is added polyethyleneimine having a molecular weight of 1800 which is further modified by ethoxylation to a degree of approximately 7 ethyleneoxy residues per nitrogen (PEI 1800, E₇) (207.3g, 0.590 mol nitrogen, prepared as in Example I) and acetonitrile (120 g). Dimethyl sulfate (28.3g, 0.224 mol) is added in one portion to the rapidly stirring solution, which is then stoppered and stirred at room temperature overnight. The acetonitrile is removed by rotary evaporation at about 60°C, followed by further stripping of solvent using a Kugelrohr apparatus at approximately 80°C to afford 220 g of the desired partially quaternized material as a dark brown viscous liquid. The ¹³C-NMR (D₂O) spectrum obtained on a sample of the reaction product indicates the absence of a carbon resonance at ~58ppm corresponding to dimethyl sulfate. The ¹H-NMR (D₂O) spectrum shows a partial shifting of the resonance at about 2.5 ppm for methylenes adjacent to unquaternized nitrogen has shifted to approximately 3.0 ppm. This is consistent with the desired quaternization of about 38% of the nitrogens.

EXAMPLE 3

Formation of amine oxide of PEI 1800 E₇

To a 500 mL Erlenmeyer flask equipped with a magnetic stirring bar is added polyethyleneimine having a molecular weight of 1800 and ethoxylated to a degree of about 7 ethoxy groups per nitrogen (PEI-1800, E₇) (209 g, 0.595 mol nitrogen, prepared as in Example I), and hydrogen peroxide (120 g of a 30 wt % solution in water, 1.06 mol). The flask is stoppered, and after an initial exotherm the solution is stirred at room temperature overnight. ¹H-NMR (D₂O) spectrum obtained on a sample of the reaction

mixture indicates complete conversion. The resonances ascribed to methylene protons adjacent to unoxidized nitrogens have shifted from the original position at ~2.5 ppm to ~3.5 ppm. To the reaction solution is added approximately 5 g of 0.5% Pd on alumina pellets, and the solution is allowed to stand at room temperature for approximately 3 days. The solution is tested and found to be negative for peroxide by indicator paper. The material as obtained is suitably stored as a 51.1% active solution in water.

EXAMPLE 4

Formation of amine oxide of quaternized PEI 1800 E₇

To a 500 mL Erlenmeyer flask equipped with a magnetic stirring bar is added polyethyleneimine having a molecular weight of 1800 which is further modified by ethoxylation to a degree of about 7 ethyleneoxy residues per nitrogen (PEI 1800 E₇) and then further modified by quaternization to approximately 38% with dimethyl sulfate (130 g, ~0.20 mol oxidizable nitrogen, prepared as in Example II), hydrogen peroxide (48 g of a 30 wt % solution in water, 0.423 mol), and water (~50 g). The flask is stoppered, and after an initial exotherm the solution is stirred at room temperature overnight. ¹H-NMR (D₂O) spectrum obtained on a sample taken from the reaction mixture indicates complete conversion of the resonances attributed to the methylene peaks previously observed in the range of 2.5-3.0 ppm to a material having methylenes with a chemical shift of approximately 3.7 ppm. To the reaction solution is added approximately 5 g of 0.5% Pd on alumina pellets, and the solution is allowed to stand at room temperature for approximately 3 days. The solution is tested and found to be negative for peroxide by indicator paper. The desired material with ~38% of the nitrogens quaternized and 62% of the nitrogens oxidized to amine oxide is obtained and is suitably stored as a 44.9% active solution in water.

EXAMPLE 5

Preparation of PEI 1200 E₇

The ethoxylation is conducted in a 2 gallon stirred stainless steel autoclave equipped for temperature measurement and control, pressure measurement, vacuum and inert gas purging, sampling, and for introduction of ethylene oxide as a liquid. A ~20 lb. net cylinder of ethylene oxide (ARC) is set up to deliver ethylene oxide as a liquid by a pump to the autoclave with the cylinder placed on a scale so that the weight change of the cylinder could be monitored.

A 750 g portion of polyethyleneimine (PEI) (having a listed average molecular weight of 1200 equating to about 0.625 moles of polymer and 17.4 moles of nitrogen functions) is added to the autoclave. The autoclave is then sealed and purged of air (by applying vacuum to minus 28" Hg followed by pressurization with nitrogen to 250 psia, then venting to atmospheric pressure). The autoclave contents are heated to 130 °C while applying vacuum. After about one hour, the autoclave is charged with nitrogen to about 250 psia while cooling the autoclave to about 105 °C. Ethylene oxide is then added to the autoclave incrementally over time while closely monitoring the autoclave pressure, temperature, and ethylene oxide flow rate. The ethylene oxide pump is turned off and cooling is applied to limit any temperature increase resulting from any reaction exotherm. The temperature is maintained between 100 and 110 °C while the total pressure is allowed to gradually increase during the course of the reaction. After a total of 750 grams of ethylene oxide has been charged to the autoclave (roughly equivalent to one mole ethylene oxide per PEI nitrogen function), the temperature is increased to 110 °C and the autoclave is allowed to stir for an additional hour. At this point, vacuum is applied to remove any residual unreacted ethylene oxide.

Next, vacuum is continuously applied while the autoclave is cooled to about 50 °C while introducing 376 g of a 25% sodium methoxide in methanol solution (1.74 moles, to achieve a 10% catalyst loading based upon PEI nitrogen functions). The methoxide solution is sucked into the autoclave under vacuum and then the autoclave temperature

controller setpoint is increased to 130 °C. A device is used to monitor the power consumed by the agitator. The agitator power is monitored along with the temperature and pressure. Agitator power and temperature values gradually increase as methanol is removed from the autoclave and the viscosity of the mixture increases and stabilizes in about 1 hour indicating that most of the methanol has been removed. The mixture is further heated and agitated under vacuum for an additional 30 minutes.

Vacuum is removed and the autoclave is cooled to 105 °C while it is being charged with nitrogen to 250 psia and then vented to ambient pressure. The autoclave is charged to 200 psia with nitrogen. Ethylene oxide is again added to the autoclave incrementally as before while closely monitoring the autoclave pressure, temperature, and ethylene oxide flow rate while maintaining the temperature between 100 and 110 °C and limiting any temperature increases due to reaction exotherm. After the addition of 4500 g of ethylene oxide (resulting in a total of 7 moles of ethylene oxide per mole of PEI nitrogen function) is achieved over several hours, the temperature is increased to 110 °C and the mixture stirred for an additional hour.

The reaction mixture is then collected in nitrogen purged containers and eventually transferred into a 22 L three neck round bottomed flask equipped with heating and agitation. The strong alkali catalyst is neutralized by adding 167 g methanesulfonic acid (1.74 moles). The reaction mixture is then deodorized by passing about 100 cu. ft. of inert gas (argon or nitrogen) through a gas dispersion frit and through the reaction mixture while agitating and heating the mixture to 130 °C.

The final reaction product is cooled slightly and collected in glass containers purged with nitrogen.

In other preparations the neutralization and deodorization is accomplished in the reactor before discharging the product.

Other preferred examples such as PEI 1200 E15 and PEI 1200 E20 can be prepared by the above method by adjusting the reaction time and the relative amount of ethylene oxide used in the reaction.

EXAMPLE 6

9.7% Quaternization of PEI 1200 E7

To a 500ml erlenmeyer flask equipped with a magnetic stirring bar is added poly(ethyleneimine), MW 1200 ethoxylated to a degree of 7 (248.4g, 0.707 mol nitrogen, prepared as in Example 5) and acetonitrile (Baker, 200 mL). Dimethyl sulfate (Aldrich, 8.48g, 0.067 mol) is added all at once to the rapidly stirring solution, which is then stoppered and stirred at room temperature overnight. The acetonitrile is evaporated on the rotary evaporator at ~60°C, followed by a Kugelrohr apparatus (Aldrich) at ~80°C to afford ~220g of the desired material as a dark brown viscous liquid. A ^{13}C -NMR (D_2O) spectrum shows the absence of a peak at ~58ppm corresponding to dimethyl sulfate. A ^1H -NMR (D_2O) spectrum shows the partial shifting of the peak at 2.5ppm (methylenes attached to unquaternized nitrogens) to ~3.0ppm.

EXAMPLE 7

Preparation of PEI 600 E₂₀

The ethoxylation is conducted in a 2 gallon stirred stainless steel autoclave equipped for temperature measurement and control, pressure measurement, vacuum and inert gas purging, sampling, and for introduction of ethylene oxide as a liquid. A ~20 lb. net cylinder of ethylene oxide (ARC) is set up to deliver ethylene oxide as a liquid by a pump to the autoclave with the cylinder placed on a scale so that the weight change of the cylinder could be monitored.

A 250 g portion of polyethyleneimine (PEI) (Nippon Shokubai, having a listed average molecular weight of 600 equating to about 0.417 moles of polymer and 6.25 moles of nitrogen functions) is added to the autoclave. The autoclave is then sealed and purged of air (by applying vacuum to minus 28" Hg followed by pressurization with nitrogen to 250 psia, then venting to atmospheric pressure). The autoclave contents are

heated to 130 °C while applying vacuum. After about one hour, the autoclave is charged with nitrogen to about 250 psia while cooling the autoclave to about 105 °C. Ethylene oxide is then added to the autoclave incrementally over time while closely monitoring the autoclave pressure, temperature, and ethylene oxide flow rate. The ethylene oxide pump is turned off and cooling is applied to limit any temperature increase resulting from any reaction exotherm. The temperature is maintained between 100 and 110 °C while the total pressure is allowed to gradually increase during the course of the reaction. After a total of 275 grams of ethylene oxide has been charged to the autoclave (roughly equivalent to one mole ethylene oxide per PEI nitrogen function), the temperature is increased to 110 °C and the autoclave is allowed to stir for an additional hour. At this point, vacuum is applied to remove any residual unreacted ethylene oxide.

Next, vacuum is continuously applied while the autoclave is cooled to about 50 °C while introducing 135 g of a 25% sodium methoxide in methanol solution (0.625 moles, to achieve a 10% catalyst loading based upon PEI nitrogen functions). The methoxide solution is sucked into the autoclave under vacuum and then the autoclave temperature controller setpoint is increased to 130 °C. A device is used to monitor the power consumed by the agitator. The agitator power is monitored along with the temperature and pressure. Agitator power and temperature values gradually increase as methanol is removed from the autoclave and the viscosity of the mixture increases and stabilizes in about 1 hour indicating that most of the methanol has been removed. The mixture is further heated and agitated under vacuum for an additional 30 minutes.

Vacuum is removed and the autoclave is cooled to 105 °C while it is being charged with nitrogen to 250 psia and then vented to ambient pressure. The autoclave is charged to 200 psia with nitrogen. Ethylene oxide is again added to the autoclave incrementally as before while closely monitoring the autoclave pressure, temperature, and ethylene oxide flow rate while maintaining the temperature between 100 and 110 °C and limiting any temperature increases due to reaction exotherm. After the addition of approximately 5225 g of ethylene oxide (resulting in a total of 20 moles of ethylene oxide per mole of PEI nitrogen function) is achieved over several hours, the temperature is increased to 110 °C and the mixture stirred for an additional hour.

The reaction mixture is then collected in nitrogen purged containers and eventually transferred into a 22 L three neck round bottomed flask equipped with heating and agitation. The strong alkali catalyst is neutralized by adding 60 g methanesulfonic acid (0.625 moles). The reaction mixture is then deodorized by passing about 100 cu. ft. of inert gas (argon or nitrogen) through a gas dispersion frit and through the reaction mixture while agitating and heating the mixture to 130 °C.

The final reaction product is cooled slightly and collected in glass containers purged with nitrogen.

In other preparations the neutralization and deodorization is accomplished in the reactor before discharging the product.

The following describe high density liquid detergent compositions according to the present invention:

TABLE I

weight %

| <u>Ingredient</u> | 8 | 9 | 10 | 11 |
|--|-------|-------|-------|-------|
| Polyhydroxy Coco-Fatty Acid Amide | 2.50 | 2.50 | -- | -- |
| C ₁₂ -C ₁₃ Alcohol Ethoxylate E ₉ | -- | -- | 3.65 | 0.80 |
| Sodium C ₁₂ -C ₁₅ Alcohol Sulfate | -- | -- | 6.03 | 2.50 |
| Sodium C ₁₂ -C ₁₅ Alcohol Ethoxylate E _{1.8} Sulfate | 20.15 | 20.15 | -- | -- |
| Sodium C ₁₄ -C ₁₅ Alcohol Ethoxylate E _{2.25} Sulfate | -- | -- | 18.00 | 18.00 |
| Alkyl N-Methyl Glucose Amide | -- | -- | 4.50 | 4.50 |
| C ₁₀ Amidopropyl Amine | 0.50 | 0.50 | 1.30 | -- |
| Citric Acid | 2.44 | 3.00 | 3.00 | 3.00 |
| Fatty Acid (C ₁₂ -C ₁₄) | -- | -- | 2.00 | 2.00 |
| NEODOL 23-9 ¹ | 0.63 | 0.63 | -- | -- |
| Ethanol | 3.00 | 2.81 | 3.40 | 3.40 |
| Monoethanolamine | 1.50 | 0.75 | 1.00 | 1.00 |

| | | | | |
|---|---------|---------|---------|---------|
| Propanediol | 8.00 | 7.50 | 7.50 | 7.00 |
| Boric Acid | 3.50 | 3.50 | 3.50 | 3.50 |
| Ethoxylated tetraethylenepentamine ² | 0.50 | -- | -- | -- |
| Tetraethylenepentamine | -- | 1.18 | -- | -- |
| Sodium Toluene Sulfonate | 2.50 | 2.25 | 2.50 | 2.50 |
| NaOH | 2.08 | 2.43 | 2.62 | 2.62 |
| Protease enzyme ³ | 0.78 | 0.70 | -- | -- |
| Protease enzyme ⁴ | -- | -- | 0.88 | -- |
| ALCALASE ⁵ | -- | -- | -- | 1.00 |
| HEDP | 0.5 | 0.7 | 2.5 | 0.5 |
| Polyamine ⁶ | 0.50 | 0.50 | -- | -- |
| Polyamine ⁷ | -- | -- | 2.00 | 1.00 |
| Water ⁸ | balance | balance | balance | balance |

1. Eg Ethoxylated Alcohols as sold by the Shell Oil Co.
2. Ethoxylated tetraethylenepentamine (PEI 189 E₁₅-E₁₈) according to U.S. 4,597,898 Vander Meer issued July 1, 1986.
3. Bleach stable variant of BPN' (Protease A-BSV) as disclosed in EP 130,756 A January 9, 1985.
4. Subtilisin 309 Loop Region 6 variant.
5. Proteolytic enzyme as sold by Novo.
6. Polyamine according to Example 7 (PEI 600 E20).
7. Polyamine according to Example 5 (PEI 1200 E20).
8. Balance to 100% can, for example, include minors like optical brightener, perfume, suds suppresser, soil dispersant, chelating agents, dye transfer inhibiting agents, additional water, and fillers, including CaCO₃, talc, silicates, etc.

TABLE II

weight %

| <u>Ingredient</u> | 12 | 13 | 14 | 15 |
|-------------------|----|----|----|----|
|-------------------|----|----|----|----|

| | | | | |
|--|---------|---------|---------|---------|
| Polyhydroxy Coco-Fatty Acid Amide | 3.65 | 3.50 | -- | -- |
| C ₁₂ -C ₁₃ Alcohol Ethoxylate E ₉ | 3.65 | 0.80 | -- | -- |
| Sodium C ₁₂ -C ₁₅ Alcohol Sulfate | 6.03 | 2.50 | -- | -- |
| Sodium C ₁₂ -C ₁₅ Alcohol Ethoxylate E _{2.5} Sulfate | 9.29 | 15.10 | -- | -- |
| Sodium C ₁₄ -C ₁₅ Alcohol Ethoxylate E _{2.25} Sulfate | -- | -- | 18.00 | 18.00 |
| Alkyl N-Methyl Glucose Amide | -- | -- | 4.50 | 4.50 |
| C ₁₀ Amidopropyl Amine | -- | 1.30 | -- | -- |
| Citric Acid | 2.44 | 3.00 | 3.00 | 3.00 |
| Fatty Acid (C ₁₂ -C ₁₄) | 4.23 | 2.00 | 2.00 | 2.00 |
| NEODOL 23-9 ¹ | -- | -- | 2.00 | 2.00 |
| Ethanol | 3.00 | 2.81 | 3.40 | 3.40 |
| Monoethanolamine | 1.50 | 0.75 | 1.00 | 1.00 |
| Propanediol | 8.00 | 7.50 | 7.50 | 7.00 |
| Boric Acid | 3.50 | 3.50 | 3.50 | 3.50 |
| Tetraethylenepentamine | -- | 1.18 | -- | -- |
| Sodium Toluene Sulfonate | 2.50 | 2.25 | 2.50 | 2.50 |
| NaOH | 2.08 | 2.43 | 2.62 | 2.62 |
| Protease enzyme ² | 0.78 | 0.70 | -- | -- |
| Protease enzyme ³ | -- | -- | 0.88 | -- |
| ALCALASE ⁴ | -- | -- | -- | 1.00 |
| HEDP | 1.5 | 1.5 | 1.5 | 0.5 |
| Polyamine ⁵ | 0.50 | 0.50 | -- | -- |
| Polyamine ⁶ | -- | -- | 2.00 | 1.00 |
| Water ⁷ | balance | balance | balance | balance |

1. E₉ Ethoxylated Alcohols as sold by the Shell Oil Co.

2. Bleach stable variant of BPN' (Protease A-BSV) as disclosed in EP 130,756 A January 9, 1985.

3. Subtilisin 309 Loop Region 6 variant.
4. Proteolytic enzyme as sold by Novo.
5. Polyamine according to Example 1 (PEI 1200 E7).
6. Polyamine according to Example 7 (PEI 600 E20).
7. Balance to 100% can, for example, include minors like optical brightener, perfume, suds suppresser, soil dispersant, chelating agents, dye transfer inhibiting agents, additional water, and fillers, including CaCO_3 , talc, silicates, etc.

TABLE III

| Ingredient | 16 | 17 | 18 | 19 |
|--|-------|-------|-------|------|
| Sodium C ₁₄ -C ₁₅ Alcohol Ethoxylate E _{2.25} Sulfate | 13.00 | -- | -- | 8.43 |
| Sodium C ₁₂ -C ₁₅ Alcohol Ethoxylate E _{2.5} Sulfate | -- | 18.00 | 13.00 | -- |
| Sodium C ₁₂ -C ₁₃ linear alkylbenzene sulfonate | 9.86 | -- | -- | 8.43 |
| Fatty Acid (C ₁₂ -C ₁₄) | -- | 2.00 | 2.00 | 2.95 |
| C ₁₂ -C ₁₃ Alcohol Ethoxylate E ₉ | -- | -- | -- | 3.37 |
| C ₁₀ Amidopropyl Amine | -- | -- | 0.80 | -- |
| NEODOL 23-9 ¹ | 2.22 | 2.00 | 1.60 | -- |
| Alkyl N-Methyl Glucose Amide | -- | 5.00 | 2.50 | -- |
| Citric Acid | 7.10 | 3.00 | 3.00 | 3.37 |
| Ethanol | 1.92 | 3.52 | 3.41 | 1.47 |
| Monoethanolamine | 0.71 | 1.09 | 1.00 | 1.05 |
| Propanediol | 4.86 | 8.00 | 6.51 | 6.00 |
| Boric Acid | 2.22 | 3.30 | 2.50 | -- |
| Ethoxylated Tetraethylenepentamine | 1.18 | 1.18 | -- | 1.48 |
| Sodium Cumene Sulfonate | 1.80 | 3.00 | -- | 3.00 |

| | | | | |
|--|---------|---------|---------|---------|
| Sodium Toluene Sulfonate | -- | -- | 2.50 | -- |
| NaOH | 6.60 | 2.82 | 2.90 | 2.10 |
| Dodecyltrimethylammonium Chloride | -- | -- | -- | 0.51 |
| Sodium Tartrate Mono and Di-succinate | -- | -- | -- | 3.37 |
| Sodium Formate | -- | -- | -- | 0.32 |
| Protease D ² | 0.88 | 0.88 | -- | -- |
| Protease subtilisin 309 variant ³ | -- | -- | 0.78 | 0.56 |
| HEDP | 0.3 | 0.7 | 1.5 | 2.5 |
| Polyamine ⁴ | 0.50 | 2.00 | -- | -- |
| Polyamine ⁵ | 1.50 | -- | 2.00 | 3.00 |
| Water ⁶ | balance | balance | balance | balance |

1. E₉ Ethoxylated Alcohols as sold by the Shell Oil Co.
2. Protease B variant of BPN¹ wherein Tyr 217 is replaced with Leu.
3. Subtilisin 309 variant having a modified amino acid sequence of subtilisin 309 wild-type amino acid sequence wherein substitutions occur at one or more of positions 194, 195, 196, 199 or 200.
4. Polyamine according to Example 4.
5. Polyamine according to Example 7.
6. Balance to 100% can, for example, include minors like optical brightener, perfume, suds suppresser, soil dispersant, chelating agents, dye transfer inhibiting agents, additional water, and fillers, including CaCO₃, talc, silicates, etc.

TABLE IV

| <u>Ingredient</u> | <u>20</u> | <u>21</u> | <u>22</u> | <u>23</u> |
|--|-----------|-----------|-----------|-----------|
| Sodium C ₁₄ -C ₁₅ Alcohol Ethoxylate E _{2.25} Sulfate | 13.00 | -- | -- | 8.43 |
| Sodium C ₁₂ -C ₁₅ Alcohol Ethoxylate E _{2.5} Sulfate | -- | 18.00 | 13.00 | -- |

| | | | | |
|---|---------|---------|---------|---------|
| Sodium C ₁₂ -C ₁₃ linear alkylbenzene sulfonate | 9.86 | -- | -- | 8.43 |
| Fatty Acid (C ₁₂ -C ₁₄) | -- | 2.00 | 2.00 | 2.95 |
| C ₁₂ -C ₁₃ Alcohol Ethoxylate E ₉ | -- | -- | -- | 3.37 |
| C ₁₀ Amidopropyl Amine | -- | -- | 0.80 | -- |
| NEODOL 23-9 ¹ | 2.22 | 2.00 | 1.60 | -- |
| Alkyl N-Methyl Glucose Amide | -- | 5.00 | 2.50 | -- |
| Citric Acid | 7.10 | 3.00 | 3.00 | 3.37 |
| Ethanol | 1.92 | 3.52 | 3.41 | 1.47 |
| Monoethanolamine | 0.71 | 1.09 | 1.00 | 1.05 |
| Propanediol | 4.86 | 8.00 | 6.51 | 6.00 |
| Boric Acid | 2.22 | 3.30 | 2.50 | -- |
| Ethoxylated Tetraethylenepentamine | 1.18 | 1.18 | -- | 1.48 |
| Sodium Cumene Sulfonate | 1.80 | 3.00 | -- | 3.00 |
| Sodium Toluene Sulfonate | -- | -- | 2.50 | -- |
| NaOH | 6.60 | 2.82 | 2.90 | 2.10 |
| Dodecyltrimethylammonium Chloride | -- | -- | -- | 0.51 |
| Sodium Tartrate Mono and Di-succinate | -- | -- | -- | 3.37 |
| Sodium Formate | -- | -- | -- | 0.32 |
| Protease D ² | 0.88 | 0.88 | -- | -- |
| Protease subtilisin 309 variant ³ | -- | -- | 0.78 | 0.56 |
| HEDP | 0.3 | 0.7 | 2.5 | 3.5 |
| Polyamine ⁴ | 0.50 | 2.00 | -- | -- |
| Polyamine ⁵ | 1.50 | -- | 2.00 | 3.00 |
| Water ⁶ | balance | balance | balance | balance |

1. E₉ Ethoxylated Alcohols as sold by the Shell Oil Co.
2. Protease B variant of BPN' wherein Tyr 217 is replaced with Leu.
3. Subtilisin 309 variant having a modified amino acid sequence of subtilisin 309 wild-type amino acid sequence wherein substitutions occur at one or more of positions 194, 195, 196, 199 or 200.

4. Polyamine according to Example 7.
5. Polyamine according to Example 1.
6. Balance to 100% can, for example, include minors like optical brightener, perfume, suds suppresser, soil dispersant, chelating agents, dye transfer inhibiting agents, additional water, and fillers, including CaCO_3 , talc, silicates, etc.

TABLE V

| Ingredients | 24 | 25 | 26 | 27 | 28 |
|---|---------|---------|---------|---------|---------|
| Polyhydroxy coco-fatty acid amide | 3.50 | 3.50 | 3.15 | 3.50 | 3.00 |
| NEODOL 23-9 ¹ | 2.00 | 0.60 | 2.00 | 0.60 | 0.60 |
| C ₂₅ Alkyl ethoxylate sulphate | 19.00 | 19.40 | 19.00 | 17.40 | 14.00 |
| C ₂₅ Alkyl sulfate | -- | -- | -- | 2.85 | 2.30 |
| C ₁₀ -Aminopropylamide | -- | -- | -- | 0.75 | 0.50 |
| Citric acid | 3.00 | 3.00 | 3.00 | 3.00 | 3.00 |
| Tallow fatty acid | 2.00 | 2.00 | 2.00 | 2.00 | 2.00 |
| Ethanol | 3.41 | 3.47 | 3.34 | 3.59 | 2.93 |
| Propanediol | 6.22 | 6.35 | 6.21 | 6.56 | 5.75 |
| Monomethanol amine | 1.00 | 0.50 | 0.50 | 0.50 | 0.50 |
| Sodium hydroxide | 3.05 | 2.40 | 2.40 | 2.40 | 2.40 |
| Sodium p-toluene sulfonate | 2.50 | 2.25 | 2.25 | 2.25 | 2.25 |
| Borax | 2.50 | 2.50 | 2.50 | 2.50 | 2.50 |
| Protease ² | 0.88 | 0.88 | 0.88 | 0.88 | 0.88 |
| Lipolase ³ | 0.04 | 0.12 | 0.12 | 0.12 | 0.12 |
| Duramyl ⁴ | 0.10 | 0.10 | 0.10 | 0.10 | 0.40 |
| CAREZYME | 0.053 | 0.053 | 0.053 | 0.053 | 0.053 |
| Optical Brightener | 0.15 | 0.15 | 0.15 | 0.15 | 0.15 |
| HEDP | 0.7 | 0.5 | 0.7 | 0.7 | 0.9 |
| Polyamine ⁵ | 1.18 | 1.18 | 1.18 | 1.18 | 1.75 |
| Fumed silica | 0.119 | 0.119 | 0.119 | 0.119 | 0.119 |
| Minors, aesthetics, water | balance | balance | balance | balance | balance |

1. C₁₂-C₁₃ alkyl E9 ethoxylate as sold by Shell Oil Co.
2. *Bacillus amyloliquefaciens* subtilisin as described in WO 95/10615 published April 20, 1995 by Genencor International.
3. Derived from *Humicola lanuginosa* and commercially available from Novo.
4. Disclosed in WO 9510603 A and available from Novo.

5. Polyamine according to Example 7.

TABLE VI

| Composition | 29 | 30 |
|--|---------|---------|
| C ₁₂₋₁₅ Alkyl sulfate | 14 | 14 |
| C ₁₂₋₁₅ Alkyl sulfate 3 ethoxylate | 4 | 4 |
| C ₁₃₋₁₅ Alkyl 7 ethoxylate | 4.5 | 4.5 |
| C ₁₂₋₁₄ alkyl glucoseamide | 4 | 4 |
| C ₈₋₁₀ alkylamidopropyl dimethylamine | 1.3 | 1.3 |
| Citric acid | 3.5 | 3.5 |
| Fatty acid | 10.5 | 10.5 |
| HEDP | 0.5 | 0.5 |
| Polyamine ¹ | 0.7 | - |
| Polyamine ² | - | 0.7 |
| Ethanol | 2 | 2 |
| 1,2 propandiol | 9 | 9 |
| Tetraethylenepentamine, 15 ethoxylate | 0.7 | 0.7 |
| Diethylenetriamine pentamethylene phosphonic acid | 0.9 | 0.5 |
| Enzymes | 2 | 2 |
| Boric acid | 2 | 2 |
| MEA (monoethanolamine) + NaOH | pH 7.5 | pH 7.5 |
| Minors, additives, water | balance | balance |

1. Polyamine of Example 7.

2. Polyamine of Example 1.

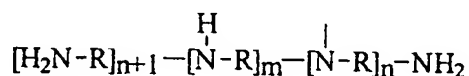
TABLE VII

| Composition | 31 | 32 | 33 | 34 | 35 |
|--|---------|---------|---------|---------|---------|
| C ₁₂₋₁₅ Alkyl sulfate, MEA salt | 10 | 14 | 16 | 16 | 15 |
| C ₁₂₋₁₅ Alkyl sulfate 3 ethoxylate, Na salt | 9 | 8 | 4 | 4 | 3 |
| C ₁₃₋₁₅ Alkyl 7 ethoxylate | 6 | 3 | - | - | 2 |
| C ₁₂₋₁₄ alkyl glucoseamide | 3 | 5 | 6 | 6 | 2 |
| C ₈₋₁₀ alkylamidopropyl dimethylamine | 1 | - | - | - | 0.5 |
| Citric acid | 1 | 3 | 2 | 2 | 5 |
| Fatty acid | 10 | 9 | 10 | 10 | 2 |
| HEDP | 1.1 | 0.7 | 2.5 | 1.5 | 2.0 |
| Polyamine ¹ | 1.5 | 1.2 | 1.5 | - | 0.5 |
| Polyamine ² | - | - | - | - | - |
| Polyamine ³ | - | - | - | 1.5 | - |
| Ethanol | 4 | 3 | 2 | 2 | 3 |
| 1,2 propandiol | 7 | 10 | 5 | 5 | 7 |
| Tetraethylenepentamine, 15 ethoxylate | 0.5 | 0.9 | - | - | 1 |
| Diethylenetriamine pentamethylene phosphonic acid | 0.5 | - | - | - | - |
| Enzymes | 1 | 3 | - | - | 3 |
| Boric acid | 3 | 1 | - | - | 3 |
| MEA(monoethanolamine)+NaOH | pH 8 | pH 8 | pH 8 | pH 8 | pH 8 |
| Minors, additives, water | balance | balance | balance | balance | balance |

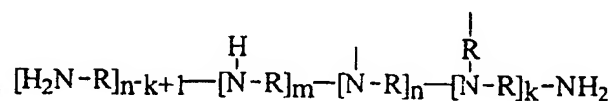
1. Polyamine of example 7.
2. Polyamine of example 1.
3. Polyamine of example 5.

CLAIMS

1. A liquid laundry detergent composition comprising a surfactant, an effective amount of HEDP, and a stabilizing amount of water-soluble or dispersible, modified polyamine comprising a polyamine backbone corresponding to the formula:

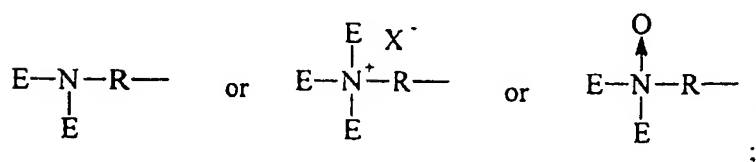


having a modified polyamine formula $V_{(n+1)}W_mY_nZ$ or a polyamine backbone corresponding to the formula:

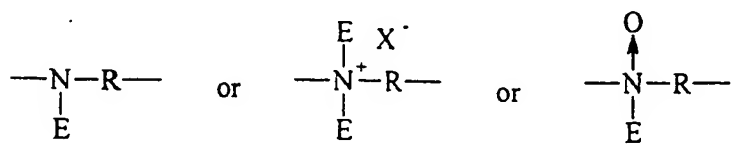


having a modified polyamine formula $V_{(n-k+1)}W_mY_nY'_kZ$, wherein k is less than or equal to n, said polyamine backbone prior to modification has a molecular weight greater than about 200 daltons, wherein

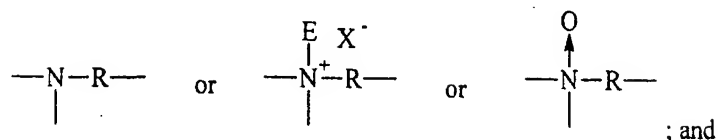
- i) V units are terminal units having the formula:



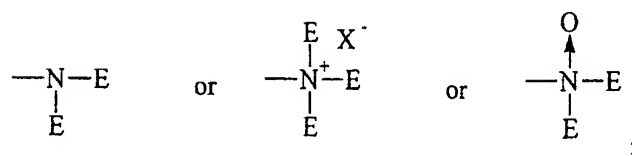
- ii) W units are backbone units having the formula:



iii) Y units are branching units having the formula:



iv) Z units are terminal units having the formula:



wherein backbone linking R units are selected from the group consisting of C₂-C₁₂ alkylene, C₄-C₁₂ alkenylene, C₃-C₁₂ hydroxyalkylene, C₄-C₁₂ dihydroxy-alkylene, C₈-C₁₂ dialkylarylene, -(R¹O)_xR¹-, -(R¹O)_xR⁵(OR¹)_x-, -(CH₂CH(OR²)CH₂O)_z-, (R¹O)_yR¹(OCH₂CH(OR²)CH₂)_w-, -C(O)(R⁴)_tC(O)-, -CH₂CH(OR²)CH₂-, and mixtures thereof; wherein R¹ is C₂-C₃ alkylene and mixtures thereof; R² is hydrogen, -(R¹O)_xB, and mixtures thereof; R³ is C₁-C₁₈ alkyl, C₇-C₁₂ arylalkyl, C₇-C₁₂ alkyl substituted aryl, C₆-C₁₂ aryl, and mixtures thereof; R⁴ is C₁-C₁₂ alkylene, C₄-C₁₂ alkenylene, C₈-C₁₂ arylalkylene, C₆-C₁₀ arylene, and mixtures thereof; R⁵ is C₁-C₁₂ alkylene, C₃-C₁₂ hydroxy-alkylene, C₄-C₁₂ dihydroxyalkylene, C₈-C₁₂ dialkylarylene, -C(O)-, -C(O)NHR⁶NHC(O)-, -R¹(OR¹)-, -C(O)(R⁴)_tC(O)-, -CH₂CH(OH)CH₂-, -CH₂CH(OH)CH₂O(R¹O)_yR¹-OCH₂CH(OH)CH₂-, and mixtures thereof; R⁶ is C₂-C₁₂ alkylene or C₆-C₁₂ arylene; E units are selected from the group consisting of hydrogen, C₁-C₂₂ alkyl, C₃-C₂₂ alkenyl, C₇-C₂₂ arylalkyl, C₂-C₂₂ hydroxyalkyl, -(CH₂)_pCO₂M-, (CH₂)_qSO₃M-, -CH(CH₂CO₂M)-CO₂M-, -(CH₂)_pPO₃M-, -(R¹O)_xB-, -C(O)R³, and mixtures thereof; provided that when any E unit of a nitrogen is a hydrogen, said nitrogen is not also an N-oxide; B is

hydrogen, C_1 - C_6 alkyl, $-(CH_2)_q-SO_3M$, $-(CH_2)_pCO_2M$, $-(CH_2)_q(CHSO_3M)CH_2SO_3M$, $-(CH_2)_q-(CHSO_2M)CH_2SO_3M$, $-(CH_2)_pPO_3M$, $-PO_3M$, and mixtures thereof; M is hydrogen or a water soluble cation in sufficient amount to satisfy charge balance; X is a water soluble anion; m has the value from 4 to about 400; n has the value from 0 to about 200; p has the value from 1 to 6, q has the value from 0 to 6; r has the value of 0 or 1; w has the value 0 or 1; x has the value from 1 to 100; y has the value from 0 to 100; z has the value 0 or 1.

2. A composition according to Claim 1 wherein said deterative surfactant comprises an anionic surfactant selected from the group consisting of alkyl alkoxy sulfate, alkyl sulfate, and mixtures thereof.
3. A composition according to Claims 1 or 2 wherein R is C_2 - C_{12} alkylene, C_3 - C_{12} hydroxyalkylene, C_4 - C_{12} dihydroxyalkylene, C_8 - C_{12} dialkylarylene, $-(R^1O)_xR^1-$, $-(R^1O)_xR^5(OR^1)_x-$, $-(CH_2CH(OH)CH_2O)_z(R^1O)_yR^1-$, $(OCH_2CH(OH)CH_2)_w-$, $-CH_2CH(OR^2)CH_2-$, and mixtures thereof.
4. A composition according to Claim 3 wherein R is C_2 - C_6 alkylene.
5. A composition according to Claim 4 wherein R is C_2 alkylene ethylene.
6. A composition according to the preceding claims wherein E is $(R_1O)_xB$.
7. A composition according to Claim 6 wherein R_1 is C_2 alkylene and B is hydrogen.
8. A composition according to Claim 7 wherein x has the value of from 5 to 30.
9. A composition according to Claim 7 wherein said PEI, prior to modification, has a molecular weight of from 200 to 3000.

10. A composition according to any of the preceding claims which comprises from 0.1% to 5% of HEDP.
11. A composition according to Claim 10 which comprises from 0.2% to 2% of HEDP.
12. A composition according to any of the preceding claims which comprises from 0.1% to 10% of said polyamine.
13. A composition according to Claim 12 which comprises from 0.2% to 5% of said polyamine.
14. A composition according to any of the preceding claims which comprises water, in amounts of less than 40%.

INTERNATIONAL SEARCH REPORT

Intern. at Application No.

PCT/IB 99/00470

| C.(Continuation) DOCUMENTS CONSIDERED TO BE RELEVANT | | |
|--|--|-----------------------|
| Category | Citation of document, with indication, where appropriate, of the relevant passages | Relevant to claim No. |
| X | WO 97 42284 A (THE PROCTER & GAMBLE CO.) 13 November 1997 see claims 1,3-5,7,10 | 1-9, 12-14 |
| A | see page 34, line 15 - line 16 see page 25, line 8 - line 21 see examples XIII-XV --- | 10,11 |
| A | EP 0 659 874 A (THE PROCTER & GAMBLE CO.) 28 June 1995 see page 4, line 1 - line 18 see page 7 see page 16, line 35 - line 40 see claims 1,7,8 ----- | 1,2,10, 11 |

INTERNATIONAL SEARCH REPORT

Information on patent family members

International Application No

PCT/IB 99/00470

| Patent document cited in search report | Publication date | Patent family member(s) | Publication date |
|---|---------------------|----------------------------|---------------------|
| WO 9742291 A | 13-11-1997 | AU 2743497 A | 26-11-1997 |
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